

CONFIGURATION INTERACTION IN THE GENERALIZED FREE ELECTRON MOLECULAR ORBITAL METHOD. II. APPLICATIONS TO THE SIX- AND FIVE-MEMBERED HETEROCYCLES CONTAINING NITROGEN ATOMS

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Ground and excited state properties of some six- and five-membered aromatic heterocycles containing nitrogen atoms have been investigated as a test for the Generalized Free Electron Molecular Orbital (G-FEMO) method with the configuration interaction procedure. Such values as the transition energies, oscillator strengths, dipole moments and charge distributions have been calculated for pyridine, pyridazine, pyrimidine, pyrazine, s-tetrazine, pyrrole, imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, 1,2,3,4-tetrazole and cyclopentadiene, the parent molecule of azoles. The results of these calculations are in good agreement with the experimental data and in some cases they are better in comparison with the results of other methods of calculation.

The present investigations indicate that the G-FEMO method with the configuration interaction procedure can be satisfactorily used in the description of the basic electronic properties of aromatic molecules containing heteroatoms.

1: Introduction

There are a few molecular orbital approaches within the framework of the π electron approximation, which are used in theoretical investigations of conjugated molecules. One of them is the Free Electron Molecular Orbital (FEMO) method (*e.g.*, Ruedenberg and Scherr 1953) applicable to conjugated hydrocarbons. This method has been generalized by Woźnicki (*e.g.*, see Woźnicki and Żurawski 1967 a, b) in such a way that it may be used satisfactorily in theoretical investigations of ground state properties of hydrocarbons as well as molecules containing heteroatoms in the conjugated bond system. In the previous paper (Żurawski 1970), hereafter referred to as I, the semiempirical method of evaluating the molecular core and electronic interaction integrals has been given. This made it possible to include the configuration interaction procedure in the Generalized Free Electron Molecular Orbital (G-FEMO) method of Woźnicki. In such form the G-FEMO method can be more satisfactorily used to interpret some excited state properties of molecules.

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To test the G-FEMO method with configuration interaction procedure, the electronic properties of azines and some five-membered molecules containing nitrogen atoms were investigated. The present paper gives the results of these investigations. In particular, the results of calculations are given for energies and oscillator strengths of transitions from the ground state to the excited singlet and triplet states, for triplet-triplet transitions and for the dipole moments and charge distributions in the ground states.

2. Outline of method

In the present investigations a given electronic state function was approximated by a linear combination of one determinantal ground state function and singly excited configuration functions. For five-membered molecules all singly excited configurations were taken into account, whereas for six-membered molecules all singly excited configuration functions were included except those in which the highest molecular orbital was occupied. Therefore, the state functions were expanded in such a way that they contained the same number of configuration functions, for all molecules under consideration. This is not any additional limitation of the method, but springs rather from the intention to describe the electronic properties of molecules by means of a minimal basis of configuration expansion.

The configuration functions are linear combinations of Slater determinants, the construction of which utilized molecular orbitals being the solutions of the one-electron equation

$$H\varphi_n = E_n\varphi_n, \quad (1)$$

where

$$H = T + V. \quad (2)$$

T denotes the kinetic energy operator and V the operator of core potential causing the motion of the π electrons.

This π electron movement was considered within a thin tube following the π electron bond path. This tube was divided into branches. Each branch was located between two neighbouring atoms in the conjugated system. According to model assumptions of the G-FEMO method, equation (1) was decomposed into equations for each branch separately. Moreover, on each branch the equation was separated into two parts, for motion of π electrons along the bond and motion across the bond.

On joining all the equations for the motion of π electrons along the bonds the one-electron eigenvalue equation of the G-FEMO method was obtained,

$$H(x)\Phi_n(x) = \varepsilon_n\Phi_n(x), \quad (3)$$

where x is the coordinate measured along the bonds. In the above equation

$$H(x) = T(x) + V(x), \quad (4)$$

where it is assumed that

$$V(x) = - \sum_{p=1}^M V_p \delta(x-x_p). \quad (5)$$

Here, x_p is the coordinate of the p -th atom contributing the π electrons to the conjugated bond system, and M is the number of such atoms. The quantity V_p is a measure of the strength of the delta type singularity associated with the p -th atom and is treated as an empirical parameter.

It was found convenient to introduce the M dimensional column vector

$$\Phi_n = \begin{bmatrix} \Phi_n(1) \\ \Phi_n(2) \\ \vdots \\ \Phi_n(M) \end{bmatrix}, \quad (6)$$

where $\Phi_n(p)$, $p = 1, 2, \dots, M$, is the value which the molecular orbital $\Phi_n(x)$ assumes at the p -th atom in the conjugated system. It was shown that all conditions which have to be imposed on the molecular orbital $\Phi(x)$ and its derivative at the points where the potential $V(x)$ is singular may be written formally in the following matrix equation

$$W\Phi_n = w_n\Phi_n. \quad (7)$$

The solution of the above eigenvalue problem for the symmetric ($M \times M$) matrix W gives the eigenvectors and the orbital energies ε_n from the formula

$$\varepsilon_n = \frac{\hbar^2}{8\pi^2 m \xi^2} \kappa_n^2, \quad (8)$$

where

$$\kappa_n = \text{ar cosh} \frac{w_n}{2}, \quad (9)$$

ξ is an arbitrary standard length (see Woźnicki and Żurawski 1967a) and m is the mass of the electron. Thus, the G-FEMO molecular orbitals $\Phi_n(x)$ are uniquely determined by the eigenvectors Φ_n and eigenvalues ε_n .

As shown in I, the molecular orbitals φ_n which are the solutions of equation (1) can be expressed as follows:

$$\varphi_n = \sum_B f(y_B, z_B) \Phi_{Bn}(x_B), \quad (10)$$

where the summation runs over all branches of a molecule. The factors $f(y_B, z_B)$ and $\Phi_{Bn}(x_B)$ describe the motion of π electrons across and along the B -th bond, respectively. Making use of this form of molecular orbitals and the orthonormalization conditions (see I), the core molecular integrals

$$I_{ik} = \int \varphi_i H \varphi_k dV \quad (11)$$

within the G-FEMO model are expressed as follows:

$$I_{ik} = (\varepsilon_k + E^{tr}) \delta_{ik}, \quad (12)$$

where the quantity E^{tr} is the same for all integrals. Since in the present investigations the ionization potentials and electron affinities were not calculated, it was not necessary to know the value of E^{tr} .

For electronic interaction molecular integrals

$$(ij|kl) = \iint \varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \varphi_k(\mathbf{r}')\varphi_l(\mathbf{r}')dVdV' \quad (13)$$

the approximations proposed in I were applied and the following expression was used for them:

$$(ij|kl) = \sum_{p,r=1}^M G(p,r) U_p^{ij} U_r^{kl}, \quad (14)$$

where $G(p,r)$ are values of function $G(R)$ for $R = R_{pq}$. For a few given interatomic distances R_{pq} they were treated as empirical parameters, whereas for the remaining they were determined by linear extrapolation. The quantities U_p^{ij} , as described in I, were calculated from the eigenvectors (6) and some simple integrals over delta atomic orbitals.

3. Geometrical structures

The structural formulae of molecules under consideration are given on Fig. 1. Unfortunately, for some molecules given on Fig. 1, experimental geometrical structures are unknown. Therefore, to dispose the similar sets of results of calculations for all molecules under considerations, assumption was made that all bond lengths and angles are equal in the given molecule. It was assumed that the interatomic distances and bond angles are equal to 1.397 Å and 120°, respectively, for six-membered molecules. On the other hand, for five-membered molecules it was assumed that the bond lengths and internal bond angles are 1.38 Å and 108°, respectively.

In addition, the calculations were made with the use of experimental geometrical structures for pyridine, pyridazine, pyrazine, s-tetrazine and pyrrole, for which these structures in the gaseous phase were known. Namely, the following gaseous geometrical structures were applied in the present calculations: for pyridine the structure¹ determined by Bak *et al.* 1958 by means of the microwave technique; for pyrazine determined by Werner *et al.* 1967 and for pyrrole by Bak *et al.* 1956 by the same microwave technique; for pyrazine, the symmetry of which precludes the microwave method, the structure proposed by Merrit and Innes 1960 in their work on rotational analysis of the near ultraviolet absorption spectrum; and for s-tetrazine that obtained by Merer and Innes 1968 by the same method as for pyrazine.

In the cases of pyrimidine and cyclopentadiene, independently of calculations for well-shaped structures, calculations were also made for a geometry which should be more probable than the well-shaped ones. Taking into consideration the experimental geometrical structures for similar molecules, it was assumed that in pyrimidine the bond lengths for the C—C and C—N bonds are equal to 1.397 Å and 1.38 Å, respectively. Such a geometrical structure

¹ The value of the C(3)—C(4) bond length in pyridine calculated from the atom coordinates obtained experimentally by Bak *et al.* 1958 differs from the value of this bond length given in the same paper. In the present investigations the value calculated from the coordinates was used.

of pyrimidine has been used in calculation of electronic properties by means of other quantum mechanical methods (see for example Woźnicki *et al.* 1964 or Pukanic *et al.* 1968). For cyclopentadiene the following bond lengths were adopted: $C(1)-C(2) = 1.53 \text{ \AA}$, $C(2)-C(3) = 1.357 \text{ \AA}$, and $C(3)-C(4) = 1.426 \text{ \AA}$. As may be seen in the subsequent

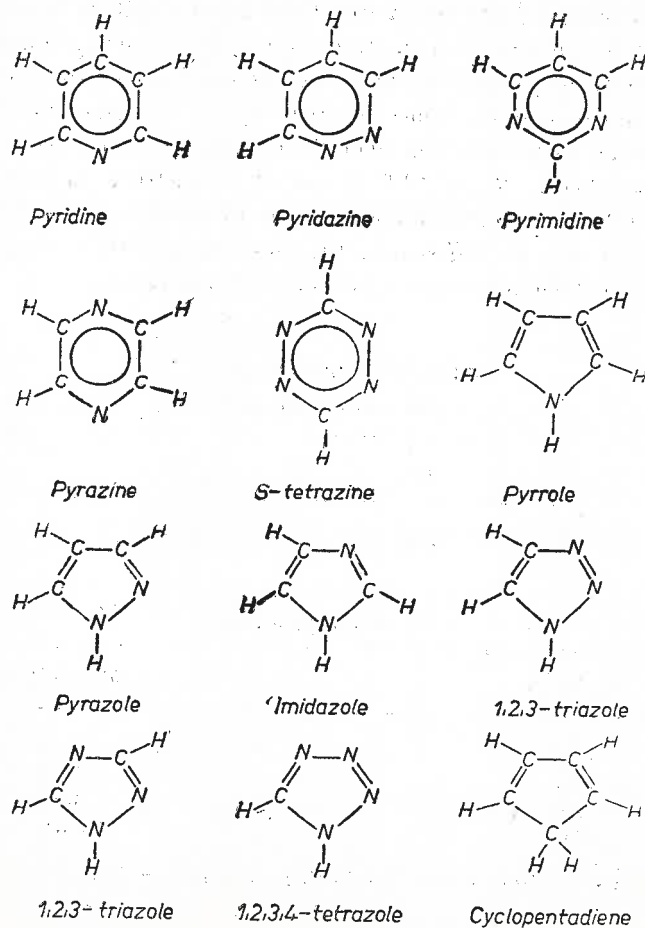


Fig. 1. The structural formulae of molecules

sections of this paper, the results of calculations with the use of such assumed geometries for these molecules are in better agreement with experimental data than those obtained with the use of well-shaped geometries.

4. Choice of empirical parameters

In the present investigations some empirical parameters appear. Namely, as mentioned in section 2, there are one-centre parameters, V_p , of which there are as many as the number of different kinds of atoms contributing π electrons to the conjugated system.

However, it was convenient to use quantities a_p instead of V_p . The quantities a_p are related to V_p by

$$a_p = \frac{8 \pi^2 m \xi}{h^2} V_p, \quad (15)$$

where for practical reasons $\xi = 1.397 \text{ \AA}$ (the C—C bond length in benzene molecule).

The remaining parameters, $G(p, q)$, are the values of the $G(R_{pq})$ function for different distances R_{pq} between the p -th and q -th centres. It was assumed that there are five such two-centre parameters $G(p, q)$, the values of which ought to be determined for the following distances: $R_{pq} = 0$ *i.e.* for the situation when the both p and q are the same centre, $R_{pq} = 1.397 \text{ \AA}$, $R_{pq} = 2.233 \text{ \AA}$, $R_{pq} = 2.420 \text{ \AA}$ and $R_{pq} = 2.794 \text{ \AA}$. However, in the case of our configuration interaction expansion the results of calculations for all molecules under consideration depend only on differences, $G(p, p) - G(p, q)$ ². Therefore, in the end only four $G(p, p) - G(p, q)$ differences appear as empirical parameters.

TABLE I

Values of empirical parameters			
One centre parameters ¹			
p	C	\dot{N}	\ddot{N}
a_p	3.950	4.114	6.150
Two-centre parameters			
R_{pq} in \AA	$G(p, p) - G(p, q)$		
1.397	4.034		
2.233	4.700		
2.420	5.399		
2.794	6.072		

¹ \dot{N} and \ddot{N} stand for the nitrogen atoms contributing one and two π electrons to the conjugated system, respectively.

The values for three of them, which correspond to three different interatomic distances in benzene and the value of a_C *i.e.* for the one-centre parameter for carbon atoms, were determined by fitting the results of calculations for $\pi - \pi^*$ transition energies in benzene to the experimental values. For these purposes the following experimental energies, 3.79 eV, 4.91 eV, 6.19 eV and 7.02 eV for transitions from the ground state $^1A_{1g}$ to excited states $^3B_{1u}$, $^1B_{2u}$, $^1B_{1u}$ and $^1E_{1u}$, respectively, were used. These experimental values were cited by Lykos 1961 as the energies of Franck-Condon maxima in benzene.

² The same situation occurs for alternant hydrocarbons for which the results of calculations by means of Pariser-Parr-Pople method depend on the differences $\gamma_{pp} - \gamma_{pq}$ in the case when only singly-excited configurations are taken into account (*e.g.* see Simons 1964).

TABLE II

Singlet π electronic transition energies (in eV) and oscillator strengths (in parenthesis) for azines

Transition	Calculated in the case of		Experimental				
	equal bonds	experimental geometrical structure	in gas	in hexane	in heptane	in H ₂ O	in cyclohexane
P y r i d i n e							
¹ B ₁ - ¹ A ₁	4.896(0.006)	5.084(0.015)	4.75 ¹ (0.04) ³	4.928(0.032) ⁴	4.8(0.030) ⁵		
¹ A ₁ - ¹ A ₁	6.175(0.001)	6.351(0.031)	6.17 ² (0.10) ³	6.276(0.122) ⁴	6.2(0.200) ⁵		
¹ A ₁ - ¹ A ₁	6.999(1.027)	7.242(0.987)	6.99 ²				
¹ B ₁ - ¹ A ₁	7.027(1.013)	7.219(0.996)	7.22 ² (1.30) ³	6.959(0.660) ⁴	7.0(1.300) ⁵		
P y r i d a z i n e							
¹ A ₁ - ¹ A ₁	4.894(0.005)	5.220(0.012)	4.9(0.02) ⁵	5.039(0.018) ⁷	5.009(0.02) ⁶		
¹ B ₁ - ¹ A ₁	6.151(0.001)	6.399(0.013)	6.2(0.10) ⁵	6.523 ⁷	6.385(0.10) ⁶		
¹ B ₁ - ¹ A ₁	7.001(1.015)	7.250(0.968)					
¹ A ₁ - ¹ A ₁	7.011(1.022)	7.420(1.039)	7.1(1.00) ⁵	6.886(0.150) ⁷			
P y r i m i d i n e							
¹ B ₁ - ¹ A ₁	4.886(0.007)	5.283(0.009) ⁸	5.0(0.05) ⁵	5.069(0.024) ⁴	5.133(0.05) ⁶	5.15 ⁹	
¹ A ₁ - ¹ A ₁	6.168(0.001)	6.494(0.029) ⁸	6.5(0.16) ⁵	6.610(0.13) ⁴	6.571(0.16) ⁶		
¹ B ₁ - ¹ A ₁	6.986(1.011)	7.374(0.990) ⁸					
¹ A ₁ - ¹ A ₁	6.998(0.993)	7.385(0.990) ⁸	7.3(1.00) ⁵	7.205(0.43) ⁴	7.315 ⁶		
P y r a z i n e							
¹ B _{3u} - ¹ A _g	4.923(0.015)	5.189(0.047)	4.8(0.100) ⁵	4.750(0.084) ⁷	4.823(0.100) ⁶	4.77 ⁹	
¹ B _{2u} - ¹ A _g	6.228(0.007)	6.405(0.103)	6.3(0.145) ⁵	6.382(0.119) ⁷	6.422(0.145) ⁶		
¹ B _{3u} - ¹ A _g	7.132(0.934)	7.423(0.954)					
¹ B _{2u} - ¹ A _g	7.031(1.093)	7.445(0.905)	7.5(1.000) ⁵	7.2 ⁷	7.315 ⁶		
S - t e t r a z i n e							
¹ B _{3u} - ¹ A _g	4.821(0.026)	5.368(0.060)	4.34 ¹⁰ 5.02 ¹¹				4.918(0.05) ¹²
¹ B _{2u} - ¹ A _g	6.122(0.003)	6.674(0.002)					
¹ B _{3u} - ¹ A _g	6.982(0.992)	7.687(0.957)					
¹ B _{2u} - ¹ A _g	6.971(1.006)	7.784(1.013)					

¹ Spomer and Rush (1952)² El-Sayed (1962)³ Pickett *et al.* (1953)⁴ Favini and Bellobono (1965)⁵ Perkin and Innes (1965)⁶ Klevens and Platt (1953)⁷ Favini *et al.* (1965)⁸ Results for assumed geometry (see text)⁹ Halverston and Hirt (1951)¹⁰ 0-0 transition, Spencer *et al.* (1961)¹¹ Maximum of absorption, Spencer *et al.* (1961)¹² Mason (1959)

The value of the parameter $G(p, p) - G(p, q)$ for $R_{pq} = 2.233 \text{ \AA}$ was determined by fitting to the experimental value 5.88 eV, being the result of calculations of energy for the ¹A₁-¹B₁ transition in pyrrole.

The values of the remaining one-centre parameters a_N and $a_{\bar{N}}$ for tertiary and secondary nitrogen atoms were calibrated from the π electron contributions to dipole moments of pyridine and pyrrole. The π electron contributions were determined by subtracting the σ electron contributions calculated by means of Slater functions (Zurawski 1966) from the experimental values of total dipole moment. This method of estimating these parameters sprang from the fact that variations in their values affect the results of calculations for transition energies less than for dipole moments.

All values of empirical parameters which were applied in the present investigations are given in Table I.

5. Energies of electronic transitions and oscillator strengths

The $\pi-\pi^*$ electronic transitions in some molecules under considerations have been investigated by different authors. In particular, there is a number of papers in which the results of calculations of electronic properties for some azines are presented. This rather large number of theoretical investigations concerning the same molecules may be justified by the fact that the calculations of electronic properties of these molecules were used the most frequently as a test for nearly all different versions of quantum chemistry methods. In the present work the calculations for azines were done from the same point of view.

The results of calculations for singlet-singlet transitions in azines are given in Table II. There are two sets of calculated transition energies and oscillator strengths for each molecule. One set for the well-shaped structure and the other for experimental geometrical structure (in the case of pyrimidine for assumed geometry). For the sake of comparison the experimental values measured in the gas phase, hexane, heptane, H_2O and cyclohexane solutions are also given. As may be seen from Table II, there is satisfactory agreement between the calculated and experimental values. Especially the calculated values for the second and third transitions agree very well with the experimental ones. The calculated transition energies for the first transitions also are in satisfactory agreement with experiments. However, their values are slightly higher than the experimental values in the case of experimental geometry. This springs probably from the fact that for azines in our configuration expansion the singly excited configurations in which the highest molecular orbitals should be occupied were omitted.

Making a comparison between the results of calculations for the well-shaped geometries and experimental ones, it may be noted that those for experimental geometries better describe the differences in the positions of particular transitions between individual molecules. It should be also noted that the oscillator strengths calculated with the use of experimental geometries are in better agreement with experimental values than those for well-shaped geometries.

Table III gives the results of calculations and experimental data for $\pi-\pi^*$ singlet electronic transition energies and oscillator strengths in cyclopentadiene and pyrrole. The agreement between theoretical and experimental values of transition energies is very good. An exception is the third transition in pyrrole, for which the calculated value is about 1 eV higher than usually cited experimental value.

TABLE III

Singlet π electronic transition energies (in eV) and oscillator strengths (in parenthesis) for cyclopentadiene and pyrrole

Transition	Calculated in the case of		Experimental		
	equal bonds and angles	experimental geometrical structure	in gas	in hexane	in EtOH
			C y c l o p e n t a d i e n e		
${}^1B_1-{}^1A_1$	4.596(0.214)	5.296(0.237) ¹	4.82 ² 5.344 ³ 5.21 ⁴	5.21 ⁵	5.21 ⁶
${}^1A_1-{}^1A_1$	5.884(0.074)	6.195(0.093) ¹	6.246 ² 6.19 ⁴		
${}^1A_1-{}^1A_1$	8.689(0.671)	9.049(0.552) ¹			
			P y r r o l e		
${}^1B_1-{}^1A_1$	5.88 ⁷ (0.344)	5.985(0.323)	5.88(0.12) ⁸ 5.88 ⁴ 5.7 ⁹		
${}^1A_1-{}^1A_1$	6.636(0.012)	6.659(0.013)	6.78(0.08) ⁸ 6.77 ⁴ 6.5 ⁹		
${}^1A_1-{}^1A_1$	8.378(0.985)	8.364(0.725)	7.25(0.60) ⁸ 7.21 ⁴ 7.1 ⁹		

¹ Results obtained for assumed geometrical structure (see text)

² 0-0 transition, Price and Walsh 1941

³ Maximum of absorption, Price and Walsh 1941

⁴ Jaffe and Orchin 1962

⁵ Scheibe 1926

⁶ Peters 1959

⁷ This value was used to calibrate the empirical parameter $G(p,p)-G(p,q)$ for $R_{pq} = 2.233 \text{ \AA}$

⁸ Pickett *et al.* 1953

⁹ Cited by Del Bene and Jaffe 1968

The calculated oscillator strengths for pyrrole predict in agreement with experiments that the second transition should be weaker than the first and third. Unfortunately, for cyclopentadiene experimental data for oscillator strengths are unavailable.

In Table IV the calculated singlet electronic transition energies and oscillator strengths for azoles are given. There are also available experimental values of transition energies obtained in different solutions. As may be seen from the table, the calculated values of transition energies are in good agreement with the experimental ones.

In all azoles the calculated oscillator strengths predict that the third transitions should be the strongest, the first transitions slightly weaker, whereas the second transitions the weakest. It should be noted that calculations for imidazole by means of the Pariser-Parr-Pople method (Fischer-Hjalmars and Nag-Chaudhuri 1969) predict the same order of oscillator strengths. Unfortunately, experimental values of oscillator strengths for these molecules are unavailable.

Table V gives the energies of transitions from the ground state to two, the lowest, triplet states for all molecules under considerations. However, experimental values are available only for pyridine, pyrimidine and pyrazine. The calculated values for these molecules are about 0.5 eV higher than the experimental ones. However, it is well known that for

The singlet π electronic transition energies (in eV) and oscillator strengths (in parenthesis) for azoles

Calculated	Experimental			
	in H ₂ O	in EtOH	in dioxane	in HCl
	Pyrazole			
5.757(0.324)	5.87 ¹	5.9—5.88 ² 5.793 ³	5.847 ⁴	5.766 ⁵
6.617(0.051)				
8.389(0.701)				
	Imidazole			
5.739(0.301)	6.0 ⁶	5.99—5.96 ⁷ 6.0 ¹⁰		
6.729(0.039)	6.45 ⁸			
8.325(0.708)				
	1,2,3-triazole			
5.714(0.301)		5.9 ⁸ 5.9 ⁹	5.82 ⁴	5.876 ⁸
6.675(0.044)				
8.294(0.708)				
	1,2,4-triazole			
5.664(0.281)				
6.686(0.054)	6.63 ¹			
8.328(0.702)				
	1,2,3,4-tetrazole			
5.766(0.320)				
6.637(0.027)				
8.226(0.711)				

¹ Mason (1963)

² Noyce *et al.* (1955)

³ Mangini and Dal Monte (1952)

⁴ Hüttel and Krantzer (1959)

⁵ Dal Monte *et al.* (1956)

⁶ Maximum of absorption, Smakula (1934)

⁷ Leandrini *et al.* (1955)

⁸ Dal Monte *et al.* (1958)

⁹ Hartel and Benson (1954)

¹⁰ Gelus and Bonnier (1967)

example in the Pariser-Parr-Pople method with the Mataga and Nishimoto 1957 approximation for electronic interaction integrals, which is the most frequently used, there are some difficulties in calculations to reproduce the triplets and singlets at the same time. Therefore, it may be regarded that there are rather satisfactory results of calculations for the transitions under consideration, judging from the very simple model applied in the present investigations.

In Table VI the energies of triplet-triplet transitions and oscillator strengths for azines are given. The letter were calculated in the case of well-shaped geometrical structures. The theory predicts a few triplet-triplet transitions for each molecule. However, for some of them the oscillator strengths are very small. Therefore, only the transitions with higher

TABLE V

Energies of transitions from the ground state to the lowest π electronic triplet states (in eV)

Molecule	Symmetry of the triplet state	Calculated for the case of		Experimental
		equal bonds	experimental geometrical structure ¹	
Pyridine	A_1	3.791	3.945	3.68 ²
	B_1	4.896	4.406	
Pyridazine	B_1	3.776	4.104	
	A_1	4.245	4.579	
Pyrimidine	A_1	3.797	4.133 ³	3.5 ⁴
	B_1	4.252	4.666 ³	
Pyrazine	B_{2u}	3.842	3.987	3.35 ⁵
	B_{3u}	4.137	4.349	
S-tetrazine	B_{2u}	3.739	4.379	
	B_{3u}	4.045	4.514	
Cyclopentadiene	B_1	1.896	2.285 ³	
	A_1	3.870	3.848 ³	
Pyrrole	B_1	2.913	3.082	
	A_1	4.891	4.775	
Pyrazole	A'	2.849		
	A''	4.867		
Imidazole	A'	2.905		
	A''	4.886		
1,2,3-triazole	A'	2.856		
	A''	4.859		
1,2,4-triazole	A'	2.882		
	A''	4.915		
1,2,3,4-tetrazole	A'	2.891		
	A''	4.847		

¹ Since the experimental geometrical structures were unknown for azoles, the energies of triplet transitions were not calculated for this case.

² Evans (1957)

³ Values obtained for the assumed geometrical structure (see text)

⁴ Loustauneau *et al.* (1963)

⁵ Value cited by Pariser and Parr (1953)

values of oscillator strengths should be observed. These predictions are confirmed for pyridazine and pyrimidine, for which the experimental data available. Moreover, the predicted values for transition energies are comparable with the experimental ones.

Energies (in eV) and oscillator strengths of the triplet-triplet transitions

Molecule	Transition	Calculated in the case of			Experimental energies
		equal bonds		experimental geometrical structure	
		Energies	Oscillator strengths	Energies	
Pyridine	${}^3A_1-{}^3A_1$	0.643 ^a	0.000	0.675	
	${}^3B_1-{}^3A_1$	1.106	0.001	0.461	
	${}^3B_1-{}^3A_1$	1.183	0.006	1.297	
	${}^3A_1-{}^3A_1$	2.975	0.097	3.163	
	${}^3B_1-{}^3A_1$	3.235	0.116	3.309	
Pyridazine	${}^3A_1-{}^3B_1$	0.468	0.0001	0.476	3.1-3.4 ¹
	${}^3B_1-{}^3B_1$	0.552	0.006	0.579	
	${}^3A_1-{}^3B_1$	1.169	0.001	1.243	
	${}^3B_1-{}^3B_1$	2.976	0.077	3.156	
	${}^3A_1-{}^3B_1$	3.249	0.105	3.353	
Pyrimidine	${}^3B_1-{}^3A_1$	0.455	0.000	0.533 ²	3.65-4.6 ¹
	${}^3A_1-{}^3A_1$	0.548	0.005	0.659 ²	
	${}^3B_1-{}^3A_1$	1.166	0.001	1.259 ²	
	${}^3B_1-{}^3A_1$	2.960	0.115	3.229 ²	
	${}^3A_1-{}^3A_1$	3.217	0.094	3.313 ²	
Pyrazine	${}^3A_g-{}^3B_{2u}$	2.849	0.115	3.277	
S-tetrazine	${}^3A_g-{}^3B_{2u}$	3.362	0.101	3.603	

¹ Loustauneau and Nouchi (1965)² For the assumed geometry (see text)

6. Dipole moments

The π electron contribution to dipole moments were calculated in order to test the usefulness of the wave functions of the G-FEMO method with the configuration interaction in the description of the remaining properties of molecules. The results for pyridine, pyridazine, pyrimidine, pyrrole, pyrazole, imidazole, 1,2,3-triazole, 1, 2, 4-triazole, 1, 2, 3, 4-tetrazole and cyclopentadiene are given in the fourth and fifth columns of Table VII.

The dipole moments of pyrazine and s-tetrazine are zero because of the symmetry of the molecules. Therefore, they were not considered.

In order to make a comparison with experiments it is necessary to add the π electron contribution to the σ electron contribution. There are several methods which give a possi-

TABLE VII

Dipole moments in Debye units

Molecule	Calculated ¹						Experimental ²			
	σ electron contribution			π electron contribution			Total	in gas	in benzene	in dioxane
	σ_x^3	σ_y^3		π_x^3	π_y^3					
Pyridine	0.0	1.243(1.513)		0.0	0.907(0.737)		2.15 ⁴ (2.25)	2.28	2.22	
Pyridazine	0.0	2.153		0.0	1.602(1.077)		2.25		3.97	
Pyrimidines	0.0	1.243		0.0	0.902(0.778)			2.00	2.44	
Pyrrrole	0.0	-0.475(0.008)		0.0	-1.365(-1.45)		1.84	1.82	1.97	
Pyrazole	-1.318	-0.047		-1.022	-0.703			1.47-1.78	2.2-2.52	
Imidazole	-0.815	-1.596		0.118	-1.993			3.87	4.02	
1,2,3-triazole	-2.133	-1.168		-0.187	-0.284			1.79		
1,2,4-triazole	-0.504	-1.168		-1.082	-1.346					
1,2,3,4-tetrazole	-1.318	-2.287		-0.985	-1.983			5.15		
Cyclopentadiene	0.0	0.0		0.0	-0.248(-0.52)		0.416	0.45		
							0.53			

¹ The results obtained for experimental geometrical structures are in parentheses.² All experimental values were taken from the compilation by Mc Clellan (1963).³ See Fig. 2 for coordinate system used.⁴ Values used for calibration of empirical parameters (see text).⁵ The values in parentheses obtained for this molecule were calculated for the assumed geometry (see text).

bility of estimating the σ electron contribution to dipole moments. One of them is the method in which the moments of lone pair electrons and bond moments are calculated theoretically with the aid of the Slater type atomic orbitals. The σ contributions to dipole moments of molecules are obtained by vector addition of the resulting bond and lone pair electrons moments.

In the present investigations this method was used. The bond dipole moments and lone pair electrons moments calculated previously (Żurawski 1966) were adopted. In particular, for C—H bond dipole moments in six-membered molecules the value of 2.304 D was used, whereas in five-membered molecules the value of 2.161 D was applied. For ter-

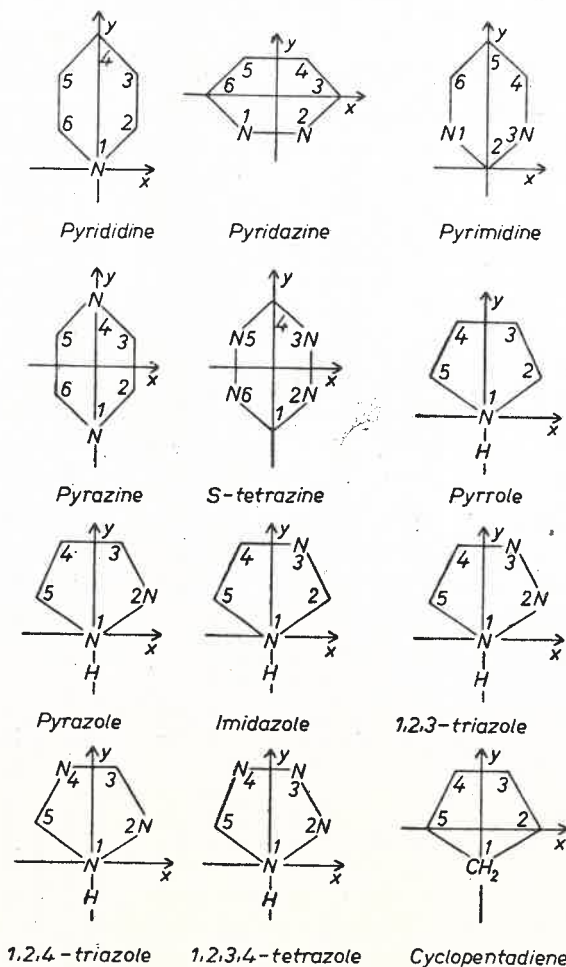


Fig. 2. The numbering and coordinate systems used

tiary nitrogen lone pair electrons moment the value of 3.547 D and for N—H bond dipole moments the value of 1.686 D were used. Moreover, it was assumed that the dipole moments of C—N bonds are equal to zero (*cf.* Hamerka and Liquori 1958).

The σ electron contributions to dipole moments of pyridine and pyrrole in the case of experimental as well as well-shaped geometrical structures were directly taken from the previous paper (Żurawski 1966).

In the case of cyclopentadiene an additional assumption was made. Namely, it was assumed that the dipole moment of CH_2 group should be approximately equal to the dipole moment of the C—H bond and ought to be situated in the plane of the molecule.

The components of σ electron contributions to dipole moments established thus are given in the second and third columns of Table VII. The coordinate systems used are given on Fig. 2. The values in parentheses in Table VII were obtained for experimental geometrical structures.

For the sake of comparison, the seventh and ninth columns of Table VII hold the available experimental values measured in the gas phase, and in benzene and dioxane solutions. These values were taken from the compilation of Mc Clellan 1963. The agreement between the calculated and experimental values is excellent. An exception is 1, 2, 3-triazole. However, this should be expected in view of the prototropic interchange.

7. Charge distributions

Making use of the definition of a charge on an atom, which has been given in I, charge distributions were calculated for all molecules under consideration. The results of these calculations for six-membered molecules are given in Table VIII. For comparison there are also given the charge distributions obtained by means of the Pariser-Parr-Pople method by Kwiatkowski and Żurawski 1965. It should be noted that there is a close correspondence between the results obtained by means of the G-FEMO method with the configuration interaction procedure and by means of Pariser-Parr-Pople method.

The charge distributions may be used as chemical reactivity indices. In particular, they are frequently applied in predicting the most sensitive position in a molecule to electrophilic substitutions. In pyridine, as is seen from Table VIII, the carbon atom in position 3 should be the most sensitive to this type of reactions. This prediction is in complete agreement with experimental data. Such electrophilic reactions as nitration, sulphonation, chlorination and mercurations give substitutions in position 3 (*e. g.*, see Ridd 1963 and Badger 1961).

In pyridazine, pyrazine and s-tetrazine the net charges on carbon atoms are positive. Therefore, the obtained charge distributions indicate that electrophilic reactions should not occur in these molecules. These predictions are in agreement with experiments (Ridd (1963), Badger 1961, Katritzky and Lagowski 1960). In general, it is known from experimental investigations that diazines are unreactive to electrophilic substitutions on carbon atoms. Pyrimidine is an exception, for electrophilic reactions occur at position 5 (*e. g.*, see the above-mentioned references). This experimental fact is predicted by the charge distributions given in Table VIII. Namely, there is negative net charge on the carbon atom at position 5.

The charge distributions in five-membered molecules are given in Table IX. Unfortunately, experimental data concerning the electrophilic substitutions in these molecules

The π electron charge distribution in azines

Molecule	Position ¹	Values of charges	
		G-FEMO	SCF ²
Pyridine	N(1)	1.066	1.160
	C(2)	0.964	0.926
	C(3)	1.006	1.010
	C(4)	0.994	0.962
Pyridazine	N(2)	1.038	1.098
	C(3)	0.965	0.927
	C(4)	0.997	0.975
Pyrimidine	C(2)	0.918	0.849
	N(3)	1.085	1.173
	C(4)	0.950	0.883
	C(5)	1.012	1.039
Pyrazine	N(1)	1.020	1.132
	C(2)	0.990	0.934
S-tetrazine	C(1)	0.928	0.866
	N(2)	1.036	1.067

¹ See Fig. 2 for numbering system used.

² From Kwiatkowski and Żurawski (1965).

are only available for cyclopentadiene, pyrrole, pyrazole and imidazole. The charge distributions in cyclopentadiene, pyrazole and imidazole predict in agreement with experimental data the most sensitive positions to electrophilic attack (*cf.* Ridd 1963). In the case of pyrrole it is known from experiments that the 2nd position is more sensitive to electrophilic substitutions than the 3rd position, whereas the charge distribution indicates position 3 as being more reactive than position 2. The situation for the pyrrole molecule has been encountered very frequently in calculations by means of another method (see *e. g.* Pilar and Morris II 1961, Julg and Carles 1962. In the calculative method used in the present investigations it is hoped that the inclusion of an inductive parameter α_{C^*} on carbon atoms adjacent to the nitrogen atom will give higher values of charges in the 2nd and 5th positions than in the 3rd and 4th. It should be noted that the inclusion of such inductive parameters was also indispensable in other, LCAO MO type, methods.

8. Conclusions

The results of calculations given in the present paper indicate that the G-FEMO method with the configuration interaction procedure described in I can be satisfactorily used for interpreting the electronic properties of ground and excited states of conjugated systems containing heteroatoms. The agreement with experimental data is rather very good.

TABLE IX

The π electron charge distribution in five-membered molecules

Molecule	Position ¹	Values of charges
Cyclopentadiene	C(1)	0.000
	C(2)	1.087
	C(3)	0.913
Pyrrole	N(1)	1.888
	C(2)	0.938
	C(3)	1.118
Pyrazole	N(1)	1.885
	N(2)	1.007
	C(3)	1.076
	C(4)	1.117
	C(5)	0.915
Imidazole	N(1)	1.886
	C(2)	0.893
	N(3)	1.180
	C(4)	1.102
	C(5)	0.939
1,2,3-triazole	N(1)	1.882
	N(2)	0.965
	N(3)	1.138
	C(4)	1.101
	C(5)	0.914
1,2,4-triazole	N(1)	1.883
	N(2)	1.014
	C(3)	1.056
	N(4)	1.178
	C(5)	0.869
1,2,3,4-tetrazole	N(1)	1.881
	N(2)	0.963
	N(3)	1.123
	N(4)	1.164
	C(5)	0.869

¹ See Fig. 2 for numbering system used.

As regards numerical results, the method proposed in I may be regarded as equivalent to the Pariser and Parr 1953 method. However, the former contains a smaller number of empirical parameters than the latter. Moreover, there is no difficulty in using one set of empirical parameters to reproduce the properties of six-membered as well as five-mem-

bered molecules, whereas in the Pariser-Parr-Pople method some troubles arise (*cf.* Fischer-Hjalmar and Sundbom 1968). It should be also noted that for some molecules*the results obtained in the present investigations are in better agreement with experiments than those obtained by means of other methods (*cf.* the results for some five-membered molecules obtained by Del Bene and Jaffé 1968).

The calculations were performed on the small Odra 1013 computer.

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