

TREATMENT OF AZA-NAPHTHALENES BY PERTURBATION METHOD

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Since the classic paper on the use of Molecular Orbital Method in the calculation of the reactivities of organic compounds by Hückel (1931) extensive work has been done in the field by Wheland and Pauling (1935), Longuet-Higgins and Coulson (1949), Dewar (1954), Pullman and Pullman (1952) and Basu (1954). From the very beginning it became clear that although for aromatic hydrocarbons the method was well suited and the calculation rather simple, in the case of compounds containing hetero-atoms like nitrogen, especially aza-hydrocarbons, the method of calculation was forbidding and the computational labour enormous, on account of the loss in symmetry of the molecule as a whole. Further, introduction of nitrogen in the molecule causes a change in the simple self-consistent field approximation since nitrogen is more electro-negative than carbon and so will have different values for coulomb and exchange integral. Although the $C-N$ bond resonance or exchange integral may be set approximately equal to that of $C-C$ bond, the coulomb integral for N cannot be considered equal to that of C even approximately. So, from the very beginning attempts have been made to devise ways out of these difficult situations. The first concrete suggestion and successful attempt was made by Wheland and Pauling (*loc. cit.*) using quantum mechanical perturbation method. They suggested that the energy levels and the wave functions of a hetero-cyclic compound may be calculated from that of the corresponding hydrocarbon if the replacement of a $=CH-$ group by a $=N-$ group be considered as a perturbation problem, such that the perturbing Hamiltonian depends on the electro-negativity parameter of nitrogen. By the extension of this method Longuet-Higgins and Coulson (*loc. cit.*) calculated the electron densities at various positions of a large number of aza-hydrocarbons and the result was found to be in good agreement with the chemical reactivity of these compounds.

Recently Dewar (*loc. cit.*) has shown that the establishment of a cross-link between two carbon atoms in the same molecule may be looked upon as a perturbation problem. Starting from the hypothetical cyclopentadecaene he calculated the energy levels and bond orders of naphthalene, which were in good agreement with the straightforward MO calculation. Success of Dewar's method opens up the possibility of simplifying the energy calculations for aza-hydrocarbons to a considerable extent. That is starting from cyclopentadecaene the introduction of nitrogen and the cross-link may be done in one step considering the process as a first order perturbation problem. That is what has been done in the present paper with naphthyridines.

It must be mentioned at the very outset that straightforward molecular orbital calculation will always give more accurate result compared to perturbation method. But as Coulson pointed out, the error introduced by perturbation method is far outweighed by the error introduced by the empirical selection of the electro-negativity parameter which is still the weak point in the MO calculation. At the same time perturbation method saves the computational labour so much that it will find favour

with experimental and theoretical physical chemists as will be evident from our calculation.

THEORY

We are not going into the detail of the Molecular Orbital calculation since good reviews on the subject are available and a recent one has been given by Basu (loc. cit.). We pass on directly to the perturbation method. The familiar equation of the first order perturbation theory is

$$W_j = \int \psi_j^* H \psi_j d\tau = W_j^0 + \int \psi_j^{0*} H' \psi_j^0 d\tau \quad \dots \quad (1)$$

where W_j = perturbed energy, W_j^0 = unperturbed energy, H' is the part of the Hamiltonian operator that refers to perturbation, and ψ_j^0 's the corresponding unperturbed molecular orbital wave functions expressed as

$$\psi_j^0 = \sum C_s \phi_s \quad \dots \quad (2)$$

where ϕ_s refers to the carbon $2p_x$ wave function. Since we have already mentioned that the perturbing Hamiltonian depends on the electron affinity of nitrogen and cross-link between carbon atoms, we may write the following expressions for the perturbing part in the energy expression (1):

$$\begin{aligned} \int \phi_j H' \phi_k d\tau &= \delta_1 \beta && \text{if } j = k = \text{position of the nitrogen} \\ &= \delta_2 \beta && \text{if } j = k = \text{carbon atoms adjacent to nitrogen} \\ &= \beta && \text{if } j \text{ and } k \text{ are cross-linked} \\ &= 0 && \text{otherwise} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (3) \end{aligned}$$

At this stage we want to comment on the term δ . Since nitrogen is more electro-negative than carbon, it will tend to draw electron from other parts of the molecule. Its electron affinity is reflected in the term δ_1 . Now as it draws electron to itself nitrogen induces a positive charge at the adjacent carbon atom which, in its turn, will attract electron from other carbon atoms and its electron affinity is indicated by the δ_2 term. It is to be admitted, however, that its magnitude will be much less than δ_1 but will be of the same sign. As this inductive effect drops off rapidly with distance we will consider only the two carbon atoms adjacent to nitrogen with respect to inductive effect. In the present calculation we have taken for δ_1 and δ_2 values 1 and 0.125 respectively. We will comment further on this point later.

In order to calculate the electron densities at various positions it is necessary to calculate the perturbed wave function for the system. Suppose in the molecule there are n orbitals of which the MOs $\psi_1, \psi_2, \dots, \psi_m$ are occupied and $\psi_{m+1}, \psi_{m+2}, \dots, \psi_n$ are unoccupied. Let us estimate what happens to the atomic orbital (AO) coefficients when the coulomb integral at r is increased by an amount $\delta\beta$. By first order perturbation theory, the perturbed wave function can be expanded in the form

$$\psi_j + \psi_j' = \psi_j + \sum_{k=1}^{n'} \left\{ \frac{\int \psi_j H' \psi_k d\tau}{W_j - W_k} \right\} \psi_k \quad \dots \quad (4)$$

where primed summation means that the term with $j = k$ is omitted and ψ_j and ψ_j' refer to the unperturbed and perturbed wave functions respectively. Substituting from equations (2) and (3) in the equation (4) we get

$$\psi_j + \psi_j' = \psi_j + \sum_{k=1}^n \left(\frac{C_{rj} C_{rk} \delta\beta}{W_j - W_k} \right) \psi_k \quad \dots \quad (5)$$

Therefore

$$\begin{aligned}\psi'_j &= \delta\beta \sum_{k=1}^n \left\{ \frac{C_{rj}C_{rk}}{W_j - W_k} \cdot \sum_s^n C_{sk}\phi_s \right\} \\ &= \sum_{s=1}^n C'_{sj}\phi_s \text{ (say)} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (6)\end{aligned}$$

Bearing in mind that the occupied orbitals are those for which $1 \leq j \leq m$, the change in electron density (q) at atom s may be written as

$$\begin{aligned}dq_s &= 2 \sum_{j=1}^m \left\{ (C_{sj} + C'_{sj})^2 - C_{sj}^2 \right\} \\ &= 4 \sum_{j=1}^m C_{sj}C'_{sj} \text{ since } C'_{sj} \text{ is small } \dots \quad \dots \quad \dots \quad (7)\end{aligned}$$

Thus

$$dq_s = 4\delta\beta \sum_{j=1}^m \sum_{k=1}^n \left(\frac{C_{rj}C_{sj}C_{rk}C_{sk}}{W_j - W_k} \right) \quad \dots \quad \dots \quad \dots \quad (8)$$

But the summand here is antisymmetric in j and k , so that $\sum_{j=1}^m \sum_{k=1}^m = 0$

therefore

$$dq_s = 4\delta\beta \sum_{j=1}^m \sum_{k=m+1}^n \left(\frac{C_{rj}C_{sj}C_{rk}C_{sk}}{W_j - W_k} \right) \quad \dots \quad \dots \quad \dots \quad (9)$$

Similarly it can be shown that the change in electron density at s due to cross-linking between atoms u and t is

$$dq_s = 2\beta \sum_{j=1}^m \sum_{k=m+1}^n \left(\frac{C_{sj}C_{sk}(C_{uj}C_{tk} + C_{uk}C_{tj})}{W_j - W_k} \right) \quad \dots \quad \dots \quad (10)$$

It is evident therefore that knowing the energy levels and electron densities of the hydrocarbon by straightforward *MO* method, the energy levels and electron densities of the system obtained by the introduction of nitrogen and cross-link at any position may be obtained by the relations (1), (3), (9) and (10).

CALCULATION

As already mentioned our calculation starts from the hypothetical cyclic polyene, cyclopentadecaene (Fig. 1). Molecular wave functions for the system are

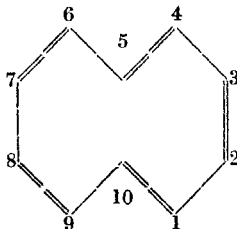


FIG. 1. Cyclopentadecaene.

approximated by a linear combination of atomic wave functions for carbon $2p_x$ electron. Solution of secular determinant for this system gives the energy values for the various molecular orbitals and is expressed as

$$E_x = E_0 + 2\beta \cos 2x\pi/k \quad \dots \quad \dots \quad \dots \quad (11)$$

and the coefficients of the atomic orbitals as

$$\psi_x = C \sum \sin n\pi x/k \cdot \phi_n \quad \dots \quad \dots \quad \dots \quad (12)$$

where E_0 is the coulomb integral, β the exchange integral, x is the particular *MO* concerned, k is equal to half the total number of atoms, n is a quantum number and can have values $0, \pm 1, \pm 2, \pm 3, \pm 4$ and 5 for the present system, and C is the normalizing factor. The energy values and the atomic orbital coefficients so calculated are given in Tables I and II respectively. In the first column of Table I are given the energy values with overlap neglected. Correction for overlap was then introduced by the method suggested by Wheland (1941) and the recalculated energies are given in column 2 of the same Table.

TABLE I
Energy levels of cyclopentadecaene

Uncorrected	Corrected
$E_0 + 2.000\beta$	$E_0 + 1.333\beta$
+1.618	+1.152
+1.618	+1.152
+0.618	+0.535
+0.618	+0.535
-0.618	-0.731
-0.618	-0.731
-1.618	-2.717
-1.618	-2.717
-2.000	-4.000

TABLE II
AO coefficients for cyclopentadecaene

State Coefficients	1	2	3	4	5	6	7	8	9	10
C_1	+0.316	+0.263	+0.362	+0.425	+0.138	+0.425	-0.138	+0.263	-0.362	-0.316
C_2	+0.316	+0.425	+0.138	+0.263	-0.362	-0.263	-0.362	-0.425	+0.138	+0.316
C_3	+0.316	+0.425	-0.138	-0.263	-0.362	-0.263	+0.362	+0.425	+0.138	-0.316
C_4	+0.316	+0.263	-0.362	-0.425	+0.138	+0.425	+0.138	-0.263	-0.362	+0.316
C_5	+0.316	+0.000	-0.447	+0.000	+0.447	+0.000	-0.447	+0.000	+0.447	-0.000
C_6	+0.316	-0.263	-0.362	+0.425	+0.138	-0.425	+0.138	+0.263	-0.362	+0.316
C_7	+0.316	-0.425	-0.138	+0.263	-0.362	+0.263	+0.362	-0.425	+0.138	-0.316
C_8	+0.316	-0.425	+0.138	-0.263	-0.362	+0.263	-0.362	+0.425	+0.138	+0.316
C_9	+0.316	-0.263	+0.362	-0.425	+0.138	-0.425	-0.138	-0.263	-0.362	-0.316
C_{10}	+0.316	-0.000	+0.447	-0.000	+0.447	+0.000	+0.447	+0.000	+0.447	+0.000

With these values the energy levels and the electron densities at various positions of aza-naphthalenes can be easily calculated from the relations (1), (2), (9) and (10). As for example the energy levels of the lowest occupied state of quinoline is obtained by introducing nitrogen at position 1 and cross-link between the positions 5 and 10 (Fig. 1) and we get

$$E_1 = E_0 + 1.333\beta + (0.316)^2\beta + 0.125\beta\{(0.316)^2 + (0.316)^2\} + \beta(0.316)(0.316) \\ = E_0 + 1.558\beta.$$

In this way the energy levels calculated for the occupied levels of various aza-naphthalenes are given in Table III. Energy levels calculated by Coulson's method are also given for comparison.

TABLE III
Occupied energy levels for various aza-naphthalenes

Position of nitrogen	Position of cross-link	Energy levels	
		Coulson	Authors
1	5-10	$E_0 + 1.584\beta$	$E_0 + 1.558\beta$
		+1.233	+1.244
		+1.163	+1.211
		+0.842	+0.722
		+0.720	+0.720
2	5-10	+1.532	+1.558
		+1.352	+1.364
		+1.035	+0.990
		+0.987	+0.885
		+0.630	+0.636
1-6	5-10	+1.707	+1.683
		+1.346	+1.335
		+1.323	+1.269
		+0.912	+0.914
		+0.883	+0.855
1-9	5-10	+1.707	+1.683
		+1.346	+1.335
		+1.323	+1.269
		+0.912	+0.914
		+0.883	+0.855
1-4	5-10	+1.707	+1.683
		+1.346	+1.335
		+1.323	+1.269
		+0.912	+0.914
		+0.883	+0.855
1-3	5-10	+1.655	+1.683
		+1.443	+1.456
		+1.218	+1.243
		+1.029	+0.826
		+0.820	+0.791
1-8	5-10	+1.655	+1.683
		+1.443	+1.456
		+1.218	+1.243
		+1.029	+0.826
		+0.820	+0.791

Electron densities calculated for various positions of the same compounds listed in Table III are given in Table IV along with those given by Longuet-Higgins and Coulson (loc. cit.).

TABLE IV
Calculated electron densities for aza-naphthalenes

Position of nitrogen	Position of cross-link	s	q_s	
			Authors*	Coulson's
1	5-10	1	1.396	1.405
		2	0.895	0.838
		3	0.993	0.998
		4	0.905	0.863
		6	0.951	0.978
2	5-10	1	0.883	0.844
		2	1.346	1.365
		3	0.926	0.943
		4	0.996	0.997
		6	1.000	1.001
1-6	5-10	1	1.347	1.383
		2	0.818	0.835
		3	0.940	0.965
		4	0.810	0.875
1-9	5-10	1	1.403	1.417
		2	0.822	0.805
		3	0.973	0.995
		4	0.866	0.841
1-3	5-10	1	1.348	1.378
		2	0.808	0.781
		3	1.324	1.363
		7	0.973	0.989
		8	0.894	0.935
1-4	5-10	1	1.322	1.383
		2	0.894	0.836
		8	0.925	0.964
		9	0.956	0.990
1-8	5-10	1	1.310	1.376
		2	0.835	0.830
		3	0.959	0.966
		4	0.881	0.865
		8	1.310	1.302

DISCUSSION

It is evident from Table III that the results obtained by simple perturbation method are in good agreement with those obtained by more exact calculation. It is also clear that when two nitrogens are introduced in a symmetrical fashion with respect to cross-link, i.e. at 1-6, 1-9 or 1-4 positions, the molecular orbital energies are not changed. Therefore for such compounds there is no change in resonance energies or absorption frequencies. Similar is the case with compounds containing unsymmetrical nitrogens, i.e. nitrogens at 1-3 or 1-8 positions. Further, since both E_0 (coulomb integral) and β (exchange integral) are negative

quantities it is evident from Table III that the energy levels of the compounds containing two nitrogens are lower than those containing one, therefore the former must be stabler than the latter. Then again, for compounds containing unsymmetrical nitrogens the energy levels are higher than those containing symmetrical ones.

Since in the above calculation no restriction has been imposed on the position of nitrogen or cross-link, we should get the same result by introducing nitrogen and cross-link at any other positions provided ultimately we get the same compound. Thus the energy levels must be the same if we introduce nitrogens at 1-9 positions and cross-link at 5-10 position or nitrogen at 2-4 positions and cross-link at 3-7 position. Calculated results for the two systems are given below :

Energy levels		Energy levels	
Nitrogen at 1-9, cross-link at 5-10	Nitrogen at 2-4, cross-link at 3-7	Nitrogen at 1-8, cross-link at 5-10	Nitrogen at 1-4, cross-link at 3-7
$E_0 + 1.683\beta$	$E_0 + 1.671\beta$	$E_0 + 1.683\beta$	$E_0 + 1.683\beta$
+1.335	+1.343	+1.456	+1.421
+1.269	+1.327	+1.243	+1.245
+0.914	+0.886	+0.826	+0.836
+0.855	+0.857	+0.791	+0.786

It is obvious that the agreement between two sets of calculations are as good as can be expected.

The total perturbing energy in these calculations was at least 2.125β which is definitely not a small quantity. In spite of that the agreement between the values obtained by perturbation method and more exact calculation is sufficient justification for the use of perturbation method in quantum chemistry.

Electron density calculations by perturbation method also agree fairly well with those given by Longuet-Higgins and Coulson (loc. cit.). Although the absolute values are slightly different the relative magnitudes are in right order and sequence.

On the assumption that the relative electron densities at various positions are of prime importance in determining the substitutive behaviour of a hetero-aromatic compound one would draw the following conclusions for the reactivity of naphthyridines from Table IV. The less the electron density at a given carbon atom the more reactive is the position to anionoid attack. Among these may be mentioned the reactivity of positions ortho and para to ring nitrogens. Amino group may be introduced at these positions easily by sodamide in liquid ammonia. The amino group in turn may be replaced by hydroxyl group which in its turn may be exchanged with chlorine by phosphorous pentachloride. Methyl group at these positions is easily oxidised to carboxyl group which in its turn is smoothly decarboxylated (Allen, 1950). All these reactions proceed through anionoid mechanism and agree fairly well with the electron densities of the positions concerned. Cationoid attack should go to the positions of high electron densities. But nitration, sulphonation, etc., of these compounds have not been effected because the electron density is highest at nitrogen where no substitution reaction can take place and attack at this position resulting in a complete decomposition of the compound.

Finally we want to comment on the use of values 1 and 0.125 in the present calculation for δ_1 and δ_2 , the electronegativity parameters for nitrogen and carbon attached to nitrogen. Wheland and Pauling (loc. cit.) by trial found out that values of 2 and 0.20 for δ_1 and δ_2 , respectively, make the calculated electron densities at various positions of pyridine agree fairly well with their chemical reactivity.

Later on it was found that with these values of δ_1 and δ_2 the calculated dipole moment (4.96D) was much too high compared to the experimental value of 2.2D. Longuet-Higgins and Coulson (loc. cit.) proposed that Pauling's suggestion actually amounts to $\frac{\delta_1}{\delta_2} = 8$. If we keep this ratio constant and change the values of δ_1 and δ_2 to those used in the present calculation we get the electron densities in agreement with the chemical reactivity and dipole moment (2.76D) close to experimental one for pyridine. But even with these values of δ_1 and δ_2 there is one great discrepancy in the calculated result. The calculated electron density at nitrogen for pyridine comes out to be less than that for quinoline whether we take for δ_1 value 1 or 2. But the basicity is in reversed order. This shows that the theory should be further developed with respect to electronegativity parameter of nitrogen and its contribution to coulomb term in *MO* calculation.

SUMMARY

An approximate method has been worked out for calculating the π -electron energy levels and the electron densities at various positions of aza-naphthalenes by simple first order perturbation method. As the parent molecule was taken the hypothetical cyclopentadecaene and the introduction of nitrogen and cross-link was considered a perturbation problem. The calculated results were in good agreement with the experimental reactivity of the molecule as well as with the result of more exact calculation.

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