An Approximate Description of the π-Electron Distribution in Pyridine, Furan, and Pyrrole as Correlated with the Molecular Model, the Dipole Moment and the Chemical Properties of these Compounds

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By the use of a postulated relationship between bond-length and number of π-electrons in C,C, C,N, and C,O bonds a calculation of the electron distribution in molecular models for pyridine, furan, and pyrrole, consistent with a large amount of numerical data from microwave investigations, has been attempted. Care has been taken to choose models in harmony with experimental dipole moments and characteristic chemical properties.

In recent publications analyses of the microwave spectra of pyridine, furan, and pyrrole and several of their deuterated species were reported [1-3]. Because of difficulties in preparing the sufficient number of isotopic molecules no unequivocal determination of the structures was possible. A few (3,2 and 2, respectively) structural degrees of freedom were still left undetermined so that only a choice of models could be given. It is the purpose of this paper to show that between the possible structures *one* can be selected in each case, reproducing the measured dipole moment and predicting the well-known chemical properties of the substances.

THEORETICAL AND EMPIRICAL BACKGROUND.

The main procedure to be used in what follows is to draw conclusions as to π-electron "contents" of a chemical bond from its measured length. For C,C bonds the formula

$$\pi = \frac{2K}{K + \dfrac{x-d}{s-x}} = \frac{0.7150}{0.3575 + \dfrac{x-1.335}{1.540-x}} \tag{I}$$

has been applied throughout. π is the number of π-electrons in the bond, x is the measured bond-length in Å, and 1.335 is the postulated distance for two atoms joined by a bond with 2 π-electrons. This number comes close to the experimental value for the length of the C,C, bond in ethylene but it need not coincide exactly with it. Also, the number 1.540 is the postulated bond-length in Å for *no* π-electrons. π-electron contents of C,O and C,N bonds are estimated by first adding 0.110, and 0.075 Å respectively to the experimental values and then using (I), a procedure which is in reasonable agreement with measured bond-lengths. The value of the constant $K = 0.3575$ was derived by letting 1.395 Å, the C,C distance in benzene, correspond to $\pi = 0.927\ e$. This is consistent with the generally accepted idea of benzene as a resonance hybrid between 78 % Kekulé-structures and 22 % Dewar-structures. The remaining $6 \times 0.073\ e$ are placed, not in the bonds, but on the carbon atoms [4]. Quite recently [5] Pritchard and Sumner have discussed the possible effects of changing K, d, and s in (I). They found that the numerical uncertainties in these parameters present no serious obstacle to the correlation of experimental and theoretical bond-lengths.

PYRIDINE

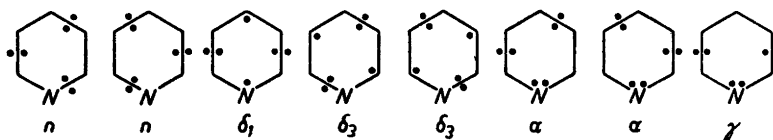The resonance structures to be taken into account are (Fig. 1):

Fig. 1. Resonance components for pyridine (hydrogens omitted). Lines indicate σ-bonds, dots represent π-electrons. n, δ_1 etc. are "mole fractions" of resonance components.

In the case of pyridine it has already been demonstrated [1] that our model V (see Table 1) must be very nearly correct. By use of bond-lengths for this model and by means of (I) it is easily calculated that $\pi(N,C) = 0.7027$; $\pi(C(2), C(3)) = 1.0256$; $\pi(C(3), C(4)) = 0.8924$. Therefore, the total charge in the six bonds amounts to 5.241 e so that the total charge on the atoms must amount to 0.7586 e. By simply counting π-electrons in the various bonds it is now easy to derive the equations (III)—(V).

$$2n + \quad \delta_1 + 2\delta_3 + 2\alpha + \quad \gamma = 1.0000 \qquad \text{(II)}$$
$$2n \qquad\quad\ + 2\delta_3 \qquad\qquad\quad = 0.7027 \qquad \text{(III)}$$
$$2n + 2\delta_1 \qquad\qquad + 2\alpha + 2\gamma = 1.0256 \qquad \text{(IV)}$$
$$2n \qquad\quad\ + 2\delta_3 + 2\alpha \qquad\quad = 0.8924 \qquad \text{(V)}$$

It follows that n = 0.3103; $\alpha = 0.0948$; $\delta_3 = 0.0410$; $\gamma + \delta_1 = 0.1076$. Now, pyridine has a measured dipole moment of 2.26 $D\downarrow$. Approximately, this moment may be thought of as consisting of a σ-moment and a π-moment (from the π-electrons). The σ-moment has been estimated[6] to 0.85 $D\downarrow$ so that the π-moment is about 1.4 $D\downarrow$. We can utilize this by setting (VI):

$$1.41 = [0.704 \times 2\alpha + 2.813\ \gamma] \times 4.802 \qquad \text{(VI)}$$

where 0.704 and 2.813 Å are the appropriate distances taken from model V. This gives $\gamma = 0.0578$. Since $\gamma + \delta_1 = 0.1076$ we get $\delta_1 = 0.0498$.

π-electron charges on the six ring-atoms may now be calculated. The charge on N is $\delta_1 + 4a + 2\gamma$ which becomes 0.5446 e. The charges on C (2), C (3), and C (4) are 0.0410, 0.0410, and 0.0498 e, respectively. Accordingly, atomic and bond charges are distributed in pyridine as shown in Fig. 2.
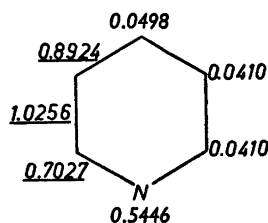
Fig. 2. Atomic and bond charges in pyridine (model V). Numbers are fractions of electronic charge. Bond charges have been underlined.

A discussion of how this model may be used in connection with a possible prediction of the fundamental chemical properties of pyridine is postponed to a following section.
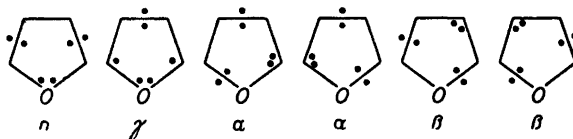
FURAN

The resonance structures used are (Fig. 3):

Fig. 3. Resonance components of furan (hydrogens omitted). Symbolism as for pyridine.
$$n + \gamma + 2a + 2\beta = 1 \; (VII).$$

The calculating procedure used above for pyridine is only applicable to some of the furan models given in Ref.[2]. For some of these models, negative values of, a, β etc. come out. Such models were discarded and a model looked for which permitted that the calculation could be carried through and also reproduced the dipole moment best possible. The finally selected model is characterized in Table 1 together with the corresponding models for pyridine and pyrrole here considered.

Table 1. Interatomic distances in the models of pyridine, furan and pyrrole applied at the calculations in this paper. Numbers in Å-units.

Distance:	Pyridine	Furan	Pyrrole
C,O		1.363	
C,N	1.342		1.387
C=C		1.362	1.367
C−C		1.442	1.428
C(2),C(3)	1.391		
C(3),C(4)	1.398		

Only models coming quite close to the models in table 1 fulfill the conditions mentioned.

Proceeding for furan as for pyridine it was found that $\pi(C,O) = 0.2958$, $\pi(C=C) = 1.4041$ and $\pi(C—C) = 0.4933$. This gives 3.8931 e in the bonds and 2.1069 e on the atoms. Furthermore

$$
\begin{aligned}
n + 2\alpha + 2\beta + \ \gamma &= 1.0000 & \text{(VII)}\\
2\alpha + 2\beta \quad\ \ &= 0.2958 & \text{(VIII)}\\
2n \quad\ + 2\beta \quad\ \ &= 1.4041 & \text{(IX)}\\
4\alpha \quad\ + 2\gamma &= 0.4933 & \text{(X)}
\end{aligned}
$$

which gives n = 0.6507; α = 0.0966; β = 0.0513; γ = 0.0535.

The experimental dipole moment of furan is 0.66 $D\uparrow$. The σ-moment has been estimated[6] to 1.30 $D\downarrow$. The expected π-moment is, therefore, 1.96 $D\uparrow$. Based on the model above one calculates a π-moment equal to (0.1932 × 0.826 + 0.1026 × 2.127) × 4.802 = 1.81 $D\uparrow$ which is rather close to 1.96 $D\uparrow$ may be closer than could ordinarily be expected.

Accordingly, atomic and bond charges are distributed in furan as shown in Fig. 4.
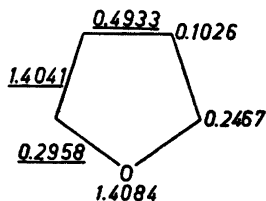

Fig. 4. Atomic and bond charges in furan (model in Table 1). Symbolism as in Fig. 2

A discussion of the chemical properties is postponed to a following section.

PYRROLE

The resonance structures considered are the same as for furan (Fig. 3). The model which could finally be selected between others that suffered from various defects has been described in Table 1. This model has $\pi(N,C) = 0.3724$; $\pi(C=C) = 1.3180$; $\pi(C—C) = 0.6020$, which means that there is 3.9828 e in the bonds and 2.0172 e on the atoms. The equations to solve are (XI—XIV):

$$
\begin{aligned}
n + 2\alpha + 2\beta + \ \gamma &= 1.0000 & \text{(XI)}\\
2\alpha + 2\beta \quad\ \ &= 0.3724 & \text{(XII)}\\
2n \quad\ + 2\beta \quad\ \ &= 1.3180 & \text{(XIII)}\\
4\alpha \quad\ + 2\gamma &= 0.6020 & \text{(XIV)}
\end{aligned}
$$

The solution is: n = 0.6190; α = 0.1462; β = 0.0400; γ = 0.0086

The experimental dipole moment of pyrrole is 1.80 $D\uparrow$. Its estimated σ-moment[6] is ~ 0.40 $D\uparrow$. Therefore, a π-moment near 1.40 $D\uparrow$ must be expected. We calculate (0.2924 × 0.8000 + 0.0800 × 2.110) × 4.802 = 1.93 $D\uparrow$, in reasonable good agreement with the expected value.

Atomic and bond charges are distributed as shown in Fig. 5.

Fig. 5. Atomic and bond charges in pyrrole (model in Table 1). Usual symbolism.
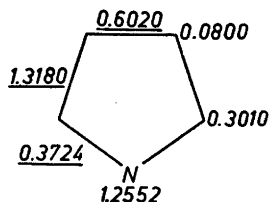
In the following section the chemical properties will be discussed.

RELATION BETWEEN π-ELECTRON DISTRIBUTION AND CHEMICAL PROPERTIES

Neither the existing theoretical background, nor the experimental evidence presented in the literature up till now permit that a rigorous discussion of this topic can be carried through. In the first place it seems certain that chemical reaction rates cannot be debated exhaustively solely by speaking of π-electron distributions. This is too often neglected in papers dealing with molecular orbital treatment of aromatic molecules. The σ-moment must also play a rôle. Secondly, this might be a minor objection as compared with the fact that the true "reaction formulae" of the partners reacting are generally more or less obscure. The following statements, therefore, only hold true to the (unknown!) extent to which all other factors of importance can be ignored.
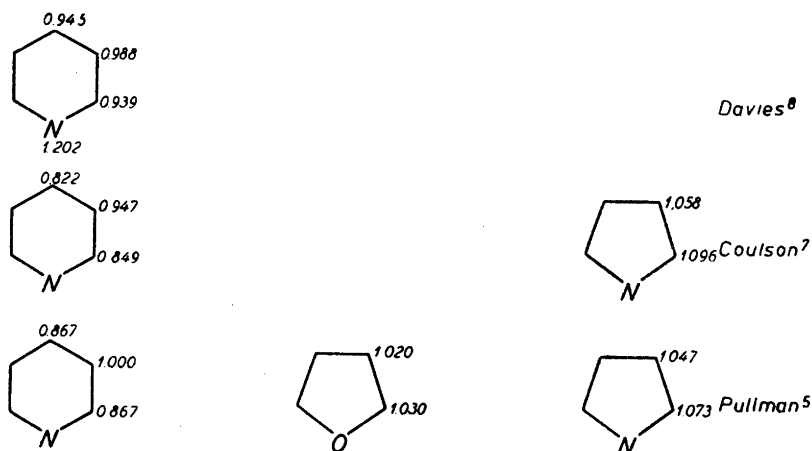

Fig. 6. Molecular diagrams found by molecular orbital treatment (Coulson and Davies) and valence-bond method (Pullman).

In the molecular orbital treatment of molecules[7] a molecular orbital is given by

$$\psi = \sum_1^n c_i\,\psi_i \qquad\qquad \sum_1^n c_i^2 = 1$$

where φ_i are *atomic* orbitals (L.C.A.O.method). For the molecules here considered $n = 6$. The six orbitals of lowest energy may be found and by summing, say, c_4^2 over all six orbitals a number is obtained which has been called the *total electronic charge* on nucleus 4. The results obtained by this procedure may be presented diagrammatically as shown in Fig. 6.

The electrons should not be thought of as almost entirely on the nuclei, but the numbers indicate the fraction of electron charge which is located at a certain atom *and* extending in the bond directions. Similar numerical data from the present investigation are obtained if the atomic charge in Figs. 2, 4, and 5 are added to *half* the charge in the adjacent bonds (not including the C,H bond). This procedure gives the diagrams of Fig. 7.
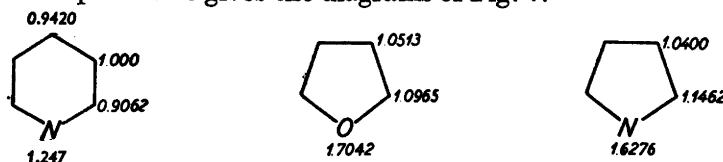

Fig. 7. Molecular diagrams from this investigation.

Taken in the usual way all diagrams of Figs. 6 and 7 equally well "explain" why pyridine prefers *electrophilic substitution*, e.g. bromination at carbon in the 3-position, and furan and pyrrole very pronouncedly react in the 2-position where the greatest electronic density is found. *Nucleophilic substitution* (e. g. amination) will be expected to take place in regions of *low* electron density. For pyridine, Pullman's and Coulson's models indicate almost equal probability for substitution in the 2- and the 4-positions in contrast to experiments which show that e. g., amination of pyridine occurs in the 2-position. This fact is somewhat more satisfactorily predicted by the diagram resulting from the present investigation.

A comparison between the calculated and "experimental" molecular diagrams is, however, not quite straightforward because the diagrams of Fig. 6 are based on molecular models which are now definitely known to be wrong (e. g. pyridine as a regular hexagon). A recalculation is intended using molecular orbital theory on more correct models.

Table 2 summarizes the results obtained.

Table 2. Weights of resonance components (in per cent) for pyridine, furan and pyrrole. Calculated and measured dipole moments (in Debye units).

	Pyridine	Furan	Pyrrole
"Classical" structure	62 %	65 %	62 %
α-ionic structures	19 %	19 %	29 %
β-ionic structure	—	10 %	8 %
γ-ionic structures	5 %	—	—
'Dewar' structures	14 %	6 %	1 %
Calculated dipole moment	2.26	0.51	2.33
Experimental —»—	2.26	0.66	1.80

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