

SHIFTS IN WAVE NUMBER OF ELECTRONIC TRANSITIONS DUE TO SUBSTITUTION—FOR FURAN, PYRROLE AND THIOPHENE

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The absorption of an organic compound is determined by two factors, first by the skeleton of unsaturated bonds and, second, by the group of radicals attached to the skeleton. The former has been studied for benzene, cyclohexadiene, fulvene and azulene by Sklar (1937). The second effect also has been studied by Sklar (1939) in the case of toluene, phenol, aniline and fluorobenzene, taking into consideration the longest wavelength region of their absorption. Sklar has concluded that the intensification of the ultraviolet absorption in substituted over unsubstituted benzene is due to partial migration of an electron to the ring or out of it. The electric moment produced by a migration of an electron from the radical into benzene ring is determined by the method of antisymmetrised molecular orbitals and the extent of migration by minimum conditions. This method of molecular orbitals which draws attention to the consequences of the migration of charges has been utilised by Herzfeld (1947) to explain the wave number shift due to substitution and calculate it in first approximation for the CH and F substituents in benzene.

Such spectral shifts have been similarly calculated in the case of aniline and methyl benzene by Ramamurthy (1954). He found a discrepancy between the calculated and the observed shifts in the case of methyl benzene and concluded that for bound electrons such as in the case of CH₃ the inductive effect should also be considered in accounting for the observed shifts. The present paper is devoted to the application of Herzfeld's method to another important class of molecules.

The theoretical investigation of the shift of the electronic transitions due to a mono-substitution, such as F, NH₂, OH and CH₃ in the case of the heterocyclic compounds, furan, pyrrole and thiophene is undertaken as a part of an extensive investigation of these compounds and their substitutions. Detailed calculations are carried out for the F and CH₃ substitutions at α and β positions on the furan, pyrrole and thiophene nuclei for the two transitions* $\phi_3 \rightarrow \phi_4$ and $\phi_3 \rightarrow \phi_5$ assuming that the shifts arise from charge migration only.

METHOD OF CALCULATION

The method adopted here for the calculation of the shift is briefly outlined below. Following Herzfeld only the migration effect, i.e. the shift in the wave number of the transition caused by a spreading of the electrons of the substituent over the whole molecule, has been considered.

Let the molecular ion into which the substitution is made be designated as the resonating system R and the substituent as X . It is assumed that there are no $\Pi-\Pi$ bonds in the substituent. An electron migrates from an occupied orbital in X to an empty orbital in R . Then the wave function of a migrating electron can be expressed as

$$\theta(\nu) = \sum A_j \phi_j(\nu) + b \xi(\nu) \quad \dots \quad (1)$$

* Nagakura and Hosoya (1952).

where $\phi_j(\nu)$ is the j th unoccupied orbital in R and $\xi(\nu)$, the occupied orbital in X . Here A_j^2 is the fraction of the electron in the substituent migrating into R and b^2 , the fraction remaining. As a result of migration, the orbital energies in R and X get modified by the coulomb contribution of the other partner. Let the values thus modified be ω_j and ω for R and X respectively.

Then

$$\begin{aligned}\omega_j &= W_j + \int \phi_j H_X \phi_j d\tau \quad \dots \quad \dots \quad \dots \quad (2) \\ \omega &= W + \int \xi H_R \xi d\tau\end{aligned}$$

where W_j (-ve) and W are the energies of ϕ_j and ξ of R and X respectively and H_R is the Hamiltonian of R including the effects of electrons therein and H_X , the Hamiltonian of X , on the removal of one electron. The change in energy* due to migration

$$U = \sum_j A_j^2 \omega_j + 2 \sum_j A_j b \rho_j + b^2 \omega - \omega \quad \dots \quad \dots \quad (3)$$

the summation being done over all unoccupied orbitals of R . The shift in wave number caused by substitution is

$$\Delta \nu = \frac{U_e - U_g}{hC} = A_n^2 \frac{(\omega - \omega_n)}{hC} - A_m^2 \frac{(\omega - \omega_m)}{hC}, \quad \dots \quad \dots \quad (4)$$

where

$$\left. \begin{aligned} A_j &= C_{j\bar{j}} \left[\frac{1}{\omega - \omega_j} \left\{ \rho' - \frac{1}{2} S \int \phi_j H_X \phi_j d\tau - S \right\} \right]; \\ \dagger \phi_j &= \sum_K (C_{j\bar{k}} p_K); \quad S = \int p_q S d\tau; \\ \text{and} \\ \rho' &= \int p_q (H_R + H_X) \xi d\tau. \end{aligned} \right\} \dots \quad \dots \quad (5)$$

(p_K being the atomic wave function of the K th atom of the ring). Treating $\int \phi_j H_X \phi_j d\tau$ in the manner of Sklar and Lyddane (1939), we get finally

$$\begin{aligned}\omega_j &= W_j - C_{j\bar{j}}^2 (aa, bb) \\ &= C_{j\bar{j}} \frac{S}{2} \left[\frac{1}{|\omega - \omega_j|} \left\{ \frac{(aa, bb)(C) + 2Q_{12}(C)}{S(C)} + \frac{ab, bb(X) + 2Q_{12}(X)}{S(X)} - \right. \right. \\ &\quad \left. \left. - C_{j\bar{j}}^2 S \left(\frac{(aa, bb)(C)}{S(C)} + \frac{(aa, bb)(X)}{S(X)} \right) - 1 \right\} \right] \quad \dots \quad (6)\end{aligned}$$

where the significance of the various integrals and explicit formulae for them are given in the papers referred to above.

APPLICATION OF THE METHOD

The above method is applied for the calculation of the shifts due to different substitutions in the case of furan, pyrrole and thiophene. As an illustration

* For further details, reference may be made to Herzfeld (1947).

† Refer to Table 1 for the various MO's.

details are given for the transition $\phi_3 \rightarrow \phi_5$ of furan due to methyl and fluorine substitution in the α -position.

From equation (4) the wave number shift due to migration of electrons from the substitution into the furan ring for $\phi_3 \rightarrow \phi_5$ transition is

$$\Delta\nu = \frac{\Lambda_3^2(\omega - \omega_3)}{hC} - \frac{\Lambda_5^2(\omega - \omega_5)}{hC}$$

where Λ_3^2 and Λ_5^2 are the extents of migration into the MO's ϕ_3 and ϕ_5 respectively. So the quantities to be evaluated are W_3 , W_5 , ω , ω_3 , ω_5 , Λ_3 , Λ_5 , of which ω can be taken to be the negative ionisation potential of the substituents and its values for CH_3 and F are -14.5 e.v. and -15 e.v. respectively.

$$\omega_3 = W_3 = C_{32}^2(aa, bb),$$

$$\omega_5 = W_5 = C_{52}^2(aa, bb),$$

where W_3 and W_5 are the energies of the corresponding MO's and C_{32} and C_{52} are

TABLE I

MO's of Furan

$$\begin{aligned} \phi_1 &= 0.6368p_1 + \frac{0.5311}{\sqrt{2}}(p_2 + p_5) + \frac{0.4969}{\sqrt{2}}(p_3 + p_4) & A_1 \\ \phi_2 &= 0.6918p_1 - \frac{0.2666}{\sqrt{2}}(p_2 + p_5) - \frac{0.6711}{\sqrt{2}}(p_3 + p_4) & A_1 \\ \phi_3 &= -\frac{0.8260}{\sqrt{2}}(p_2 - p_5) - \frac{0.5636}{\sqrt{2}}(p_3 - p_4) & B_1 \\ \phi_4 &= 0.2249p_1 - \frac{0.8035}{\sqrt{2}}(p_2 + p_5) + \frac{0.5503}{\sqrt{2}}(p_3 + p_4) & A_1 \\ \phi_5 &= -\frac{0.5635}{\sqrt{2}}(p_2 - p_5) + \frac{0.8258}{\sqrt{2}}(p_3 - p_4) & B_1 \end{aligned}$$

MO's of Pyrrole

$$\begin{aligned} \phi_1 &= 0.5223p_1 + \frac{0.6186}{\sqrt{2}}(p_2 + p_5) + \frac{0.5781}{\sqrt{2}}(p_3 + p_4) & A_1 \\ \phi_2 &= -0.7750p_1 + \frac{0.03959}{\sqrt{2}}(p_2 + p_5) + \frac{0.6305}{\sqrt{2}}(p_3 + p_4) & A_1 \\ \phi_3 &= -\frac{0.8328}{\sqrt{2}}(p_2 - p_5) - \frac{0.5539}{\sqrt{2}}(p_3 - p_4) & B_1 \\ \phi_4 &= 0.3573p_1 - \frac{0.7954}{\sqrt{2}}(p_2 + p_5) + \frac{0.4893}{\sqrt{2}}(p_3 + p_4) & A_1 \\ \phi_5 &= +\frac{0.5544}{\sqrt{2}}(p_2 - p_5) - \frac{0.8322}{\sqrt{2}}(p_3 - p_4) & B_1 \end{aligned}$$

TABLE 1—*contd.**MO's of Thiophene*

$$\begin{aligned} \phi_1 &= 0.3850p_1 + \frac{0.6068}{\sqrt{2}}(p_2+p_5) + \frac{0.6952}{\sqrt{2}}(p_3+p_4) & A_1 \\ \phi_2 &= -\frac{0.8390}{\sqrt{2}}(p_2-p_5) - \frac{0.5443}{\sqrt{2}}(p_3-p_4) & B_1 \\ \phi_3 &= -0.8017p_1 - \frac{0.1531}{\sqrt{2}}(p_2+p_5) + \frac{0.5781}{\sqrt{2}}(p_3+p_4) & A_1 \\ \phi_4 &= 0.4597p_1 - \frac{0.7775}{\sqrt{2}}(p_2+p_5) + \frac{0.4295}{\sqrt{2}}(p_3+p_4) & A_1 \\ \phi_5 &= +\frac{0.5441}{\sqrt{2}}(p_2-p_5) - \frac{0.8389}{\sqrt{2}}(p_3-p_4) & B_1 \end{aligned}$$

the coefficients of the A.O. on carbon atom 2 in furan in the *MO's ϕ_3 and ϕ_5 respectively, the position of carbon atom 2 being the α -position. The values (Table 3) of W_3 and W_5 are taken from the results of Nagakura and Hosoya (1952). The values of C_{32} and C_{52} are adopted here from calculations made by the author using the data given by Nagakura and Hosoya. The evaluation of the quantities A_3 and A_5 involves the calculation of the integrals occurring in expression (6). Of these, the energy integrals (aa , bb), (ab , bb) and Q_{12} are calculated by Parr and Crawford (1948) from the pertinent formulae given by Sklar (1939). These are taken over into the present calculations. All the pertinent overlap integrals S , $S(C)$ and $S(x)$ are calculated by the author from the master formulae given by Mulliken *et al.* (1949).

TABLE 2

Furan			Pyrrole			Thiophene		
B_1	ϕ_5	2.599 β	B_1	ϕ_5	2.566 β	B_1	ϕ_5	2.499 β
A_1	ϕ_4	3.174 β	A_1	ϕ_4	3.026 β	A_1	ϕ_4	2.908 β
B_1	ϕ_3	4.488 β	B_1	ϕ_3	4.453 β	A_1	ϕ_3	4.360 β
A_1	ϕ_2	5.364 β	A_1	ϕ_2	4.876 β	B_1	ϕ_2	4.512 β
A_1	ϕ_1	6.515 β	A_1	ϕ_1	6.429 β	A_1	ϕ_1	6.221 β

RESULTS

The calculated data are collected in Table 3 in which the last row gives the value of the shift for α -methyl and α -fluoro substitution in furan for the $\phi_3 \rightarrow \phi_5$ transition.

* The complete set of MO's are given in Table 1.

TABLE 3*

	α -methyl furan	α -fluoro furan		α -methyl furan	α -fluoro furan
W_3 ..	4.488β	4.488β	A_3^2	0.2937	0.06585
W_6 ..	2.599β	2.599β	A_6^2	0.0699	0.01545
C_{32} ..	$0.8260/\sqrt{2}$	$0.8260/\sqrt{2}$	$\Delta\nu$	-2708 cm. ⁻¹	-406 cm. ⁻¹
C_{52} ..	$0.5635/\sqrt{2}$	$0.5635/\sqrt{2}$			

Similar calculations have been made for the shifts due to methyl and fluorine substitution in the β -position for the different electronic transitions for the three compounds. The values of the shifts are presented in Table 4.

TABLE 4

(Shifts in cm.⁻¹)

Transition	Furan		Pyrrole		Thiophene	
	α	β	α	β	α	β
<i>Methyl Substitution</i>						
$\phi_3 \rightarrow \phi_4$..	-1145	-333	-1302	-501	1989	797
$\phi_3 \rightarrow \phi_5$..	-2708	1388	-2787	1290	853	1101
<i>Fluorine Substitution</i>						
$\phi_3 \rightarrow \phi_4$..	-170	-50	-203	-73	190	-399
$\phi_3 \rightarrow \phi_5$..	-406	166	-423	180	-18	-115

DISCUSSION

A few interesting features emerging out of the above calculations may be pointed out here.

(1) In furan and pyrrole the electrons occupying the MO ϕ_3 will be mainly on the four carbon atoms of the ring, whereas in the case of thiophene they are distributed on all the five ring atoms including the hetero atom, sulphur. On the other hand the electrons occupying the MO ϕ_2 will be distributed on all the five atoms of the ring, in the case of furan and pyrrole, while in thiophene they are confined only to four carbon atoms. Hence a transition such as $\phi_3 \rightarrow \phi_4$ for furan and pyrrole should be similar to $\phi_2 \rightarrow \phi_4$ for thiophene with regard to the shift. This is evident for the calculated values of the shifts in the different cases. For example from Table 4 the shifts are negative for α as well as β (substituents being either CH₃ or F) and similar

* The values given in Table 3 are those calculated using only $\xi_1 = \eta(\psi_{C1} + \psi_H)$ as the orbital of the substituent; however, the shift $\Delta\nu$ is the effect considering all the three sp^3 hybridised wave functions.

negative shifts are obtained for α and β substituents in thiophene for the transition $\phi_2 \rightarrow \phi_4$, these are

Thiophene				
		α	β	
F	-256 cm. ⁻¹	-99 cm. ⁻¹
CH ₃	-1895 cm. ⁻¹	-656 cm. ⁻¹

(2) The effect of substitution on the H atom of the imino group in pyrrole on the electronic transitions is another interesting feature.

(a) Consider the transition $\phi_3 \rightarrow \phi_4$. As has already been pointed out that the electrons occupying the MO ϕ_3 will spend mainly on the carbon atoms of the ring, the fraction contributed to the hetero atom N being nil. From the formula (4) the shift is dependent mainly on two factors.

- (i) A_3^2 , the fraction of electron migrating into the orbital ϕ_3 when the substitution is made on the H atom of the NH group, i.e. on the atom 1. Fig. 1 is dependent on the coefficient of the wave function of atom 1.

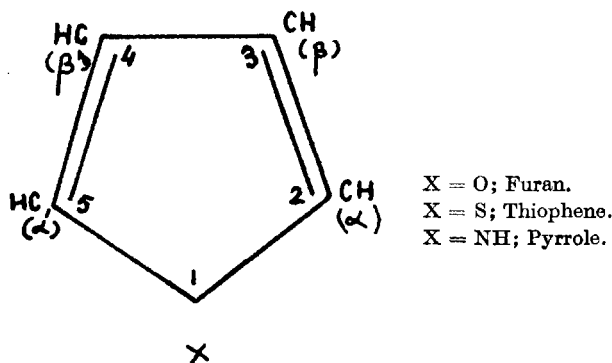


FIG. 1.

X = O; Furan.
X = S; Thiophene.
X = NH; Pyrrole.

- (ii) A_4^2 , the fraction of electron migrating into the orbital ϕ_4 , is dependent on the coefficient of the wave function of atom 1 in that MO. For this transition it is seen $A_3^2 = 0$. Hence the shift is entirely determined by $-A_4^2(\omega - \omega_4)$. The shift is either towards the violet or towards the red according as $(\omega - \omega_4)$ is negative or positive. This holds good for any substitution on H atom of NH group of pyrrole for the transition $\phi_3 \rightarrow \phi_4$, provided of course the migration effect alone is taken into account.

(b) Consider the transition $\phi_3 \rightarrow \phi_5$. In this case both A_3^2 and A_5^2 will be zero, if the substitution is made on the H atom of NH group. Hence the spectrum of any N-substituted pyrrole for this transition should lie in the same position as of the parent molecule, i.e. the shift is zero.

(3) An effective comparison of the calculated shifts with the observed values is not possible at present, since sufficiently extensive experimental data on the absorption of furan, pyrrole and thiophene substitutions are not available. The author has found it difficult to obtain pure samples of several of these compounds. Observations made in a few cases by the author may be mentioned here.

(a) *Thiophene substitutions*

Three band systems have been analysed in the vapour absorption spectrum of thiophene by Milazzo (1947) with *O, O* bands at ν 41595 cm.^{-1} , 42992 cm.^{-1} and 45378 cm.^{-1} ascribed to the transitions *A-B*, *A-B'* and *A-C* respectively. It is not definite which of the bands 41595 cm.^{-1} or 42992 cm.^{-1} is to be assigned to the transition $\phi_3 \rightarrow \phi_5$ (*A*₁-*B*₁) for which the calculated position according to Nagakura and Hosoya is about 42630 cm.^{-1} (probably it is ν 42992). The calculated shifts for this transition for the α -methyl thiophene and β -methyl thiophene are respectively 853 cm.^{-1} and 1101 cm.^{-1} . The shifts are positive and towards the violet. One would expect therefore absorption in α -methyl substituted thiophene at ν 42448 or more probably at 43845 cm.^{-1} . Absorption observations are made on α -methyl thiophene in the vapour condition. Photographs of the absorption spectrum are taken on the medium quartz spectrograph in region down to λ 2200. No trace of discrete absorption has been detected. There is, however, a continuous cut off of the spectrum down towards the violet, commencing from a wavelength in the region λ 2600 to λ 2440 depending on the physical conditions like temperature, vapour pressure and length of the absorbing column. Exact verification of the shift of the band system is therefore not possible. For alkyl thiophenes Appleby and others (1940) have reported in the solution phase maxima of absorption between $\lambda\lambda$ 2300 and 2400. If for 2-methyl thiophene, in the vapour phase a similar absorption in the same region may be presumed, an approximate agreement between the predicted and observed shifts may be taken.

An exactly similar situation is observed in the case of β -methyl substitution also in which case too no discrete absorption has been observed down to λ 2200.

It is expected that a close agreement would exist between the observed and calculated shifts in the case of α -fluoro, β -fluoro thiophenes, since for fluoro benzene, Herzfeld's calculation agrees well with the observed value indicating in this case that the migration effect mainly determined the shift of the absorption band. Unfortunately neither of these compounds could be obtained. It would be of interest if one observes the absorption of either of these compounds.

(b) *Pyrrole substitutions*

Experimental verification of the shifts in case of pyrrole substitutions also has not been possible as none of the substituted compounds could be obtained.

(c) *Furan substitutions*

The calculated value of the shift for the transition $\phi_3 \rightarrow \phi_5$ in furan for a CH_3 in the α -position is -2708 cm.^{-1} . For this transition, the *O-O* band is located at ν 52230 by Pickett. If the assumption made in the calculation of the shift is correct (i.e. the shift depending on the migration effect alone), the *O-O* band of this transition in α -methyl furan and $\alpha\alpha'$ -dimethyl furan should be expected at approximately ν 49500 and 46800 respectively. The absorption of α -methyl furan has been investigated by the author under various experimental conditions. A faint but definite discrete absorption is found at ν 42700, although an extensive band system has not been obtained. If the *O-O* band is to be located in this region, there is a large discrepancy between the observed and calculated positions (observed 42700, calculated 49522).

The discrepancy is equally large when the calculated and the observed positions are compared for the $\alpha\alpha'$ (2, 5) dimethyl furan in which the *O-O* band is located at ν 40541, the calculated shift being ν 46814. The conclusion seems to be that for a CH_3 substitution where bond electrons are involved, the migration effect alone does not give the entire shift, inductive effect may be an equally if not more predominant factor in determining the total shift.

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SUMMARY

Shifts in wave numbers for two of the electronic transitions in furan, pyrrole and thiophene due to fluorine and methyl (mono) substitutions both in α and β positions are calculated, considering migration of the charges from the substituent into the ring alone. The same method is extended to a disubstituted compound— $\alpha\alpha'$ -dimethyl furan. Similar shifts have also been discussed when the substitution is made on the H atom of the imino group in pyrrole. A discussion with regard to the magnitude and nature of the shifts is presented.

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