THEORETICAL CALCULATION OF SHIFTS IN SUBSTITUTED BENZENES

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ABSTRACT. Using the M. O. method of Herzfeld the effect of CH_3 and NH_2 substitutions in benzene in shifting the o,o position of the band system of benzene has been calculated. It is suggested that the inductive effect is also to be taken into account.

INTRODUCTION

It was pointed out by Herzfeld (1947) that the M. O. method can be applied to the computation of the wavelength shift of the o,o position of the band system consequent on substitution in molecules with conjugated π bonds. Herzfeld performed the calculation for F and OH substitutions in benzene. For the F substitution the calculated value was somewhat agreeing with the observed shift. For OH, however, the difference was large, being only slightly less than 30 % of the experimental value.

There are two principal effects of substitution—"migration of charge into the ring" and "the inductive effect". In Herzfeld's computations, the migration effect alone was considered. This was in accordance with Sklar's (1939) empirical estimate of the importance of the two effects in relation to the intensification of the spectra consequent upon substitution.

HERZFELD'S METHOD

If ϕ_j be the jth M.O. of the ring, ζ of the substituent, then neglecting charge distortion in the ring by the substitution, the ring electrons will be in orbitals ϕ_j, and the electrons in the substituent will, in the substituted compound, be in the orbitals $\Sigma \Lambda_j \phi_j + b\zeta$. Λ_j's define the extent of migration of the substituent electrons into the ring. Normalisation requirement leads to the expression

$$\Sigma \Lambda_j^2 + 2 \Sigma \Lambda_j b S_j + b^2 = 1 \text{ where } S_j = \int \phi_j \zeta d\tau \qquad \dots \quad (1)$$

The energy of the molecule will be $\int \psi * H \psi d\tau$ where ψ is the wavefunction for the whole molecule, obtained by multiplying the orbitals for the various electrons, antisymmetrising and normalising. This can be shown to be equal to

$$\Sigma \Lambda_j^2 \omega_j + 2 \Sigma \Lambda_j b \rho_j + b^2 \omega$$

(summation over unfilled orbitals). Here ω, ω_j are the energies of the

orbital in the substituent and the ring respectively as modified by the perturbation of the other, and p_j is the exchange integral. The energy in substituent, however, is ω. The energy change is then

$$U = \Sigma \Lambda_j{}^2 \omega_j + 2\Sigma \Lambda_j b p_j + b^2\omega - \omega \qquad \qquad \dots \quad (2)$$

Minimising this, in the light of (1), leads to

$$\Lambda_j = -\frac{p_j - \omega S_j}{\omega - \omega_j} \qquad \qquad \dots \quad (3)$$

putting $b \asymp 1$. Substituting (3) in (2)

$$U = \Sigma(\omega - \omega_j)\Lambda_j{}^2$$

Now, considering an electronic transition, in the ground state all orbitals upto a certain n are filled up, only the remaining are available for migration $(j > n)$ and

$$U_g = \sum_{j > n} (\omega - \omega_j)\Lambda_j{}^2$$

whereas in the excited state one electron of orbital n is raised to a higher orbital ϕ_m $(m > n)$ (say). The orbital ϕ_m is thus "half closed" for migration and the orbital ϕ_n is "half opened" for it. The same might be thought of as complete closing up of ϕ_m for immigration of electrons and complete opening up of ϕ_n for the same process ; and change in the excited energy level consequent upon migration is

$$U_e = \Lambda_n{}^2(\omega - \omega_n) + \sum_{j > n} (\omega - \omega_j)\Lambda_j{}^2 - (\omega - \omega_m)\Lambda_m{}^2$$

The wavenumber shift is then

$$\Delta\nu = \frac{U_e - U_g}{hc} = \Lambda_n{}^2 \frac{\omega - \omega_g}{hc} - \Lambda_m{}^2 \frac{\omega - \omega_m}{hc} \qquad \dots \quad (4)$$

To compute the quantities occurring in (4) a number of simplifying assumptions are made, e.g., the distance between the carbon atom and the substituent is unaltered by excitation to a higher level, similarly overlap integrals between non-neighbouring atoms are negligible. It proves possible to write

$$\Lambda_j = c^j \left\{ \frac{1}{\omega - \omega_j} \middle| \rho' - \frac{1}{2} S \int \phi_j H \times \phi_j d\tau \right] - \frac{S}{2} \right\} \qquad \dots \quad (5)$$

using (3) above and writing $S_j = c_s{}^{(j)}S, \quad S = \int ps\zeta d\tau,$

$$p_j = c_s{}^{(j)}[\rho' + \tfrac{1}{2}S(\omega + \omega_j)],$$

$$2\rho' = \int p_s(H_R + H_X)\zeta d\tau$$

with Herzfeld. Here $c_s{}^{(j)}$ is the coefficient of p_s, the $2p\pi$ A. O. of sth atom, in ϕ_j. ω, ω_j are the energies of ζ, ϕ_j respectively. The notation is the same as in Herzfeld's paper. In (5) all the quantities can be computed (Herzfeld's formulae 27, 28, 29) using the values of integrals given by Sklar and Lyddane (1939).

APPLICATION TO CH_3 AND NH_2 SUBSTITUTIONS

· This method has now been applied for the CH_3 and NH_2 substitutions in benzene. In doing this the fact that the migrating electrons are coming from the hybridised orbitals in the substituent is remembered in the evaluation of the overlap integrals from formulae (23) Sklar's paper (1939).

The ionisation potentials of the radi ls in the compounds, and the electron affinity of the methyl radical, e taken from the same paper. The values of the integrals (excepting $_{22}$) are obtained by graphical plotting from the values given in Sklar and Lyddane's paper (1939). Q_{22} has been calculated directly from formula (18). For methyl group the overlap integrals have been taken from Mulliken, Rieke and others (1948-49).

These results together with those of Herzfeld for F and OH are tabulated below. For CH_3 substitution the figure given is the resultant red shift for all the three orbitals in the substituent.

TABLE I

Molecule	Calculated red shift	Observed red shift
C_6H_5F	−230	−271
C_6H_5OH	−1170	−1730
C_6H_5NH	−1964	−4055
$C_6H_5CH_3$	−44.38	−605

DISCUSSION

In discussing the results it should be kept in view that in CH_3 substitution there are no unbound electrons. In the other molecules the migration of only the unbound electrons is considered. But in $C_6H_5CH_3$ only the migration of bound electrons can be considered. If an orbital in the substituent is ζ and the orbitals in the ring be ϕ_j. then, in the substituted compound, neglecting inductive effect, the electron in the substituent will be in the orbitals

$$\Sigma \Lambda_j \phi_j + b \zeta$$

Λ_j's here define the extent of migration of the substituent electron from orbital ζ into orbitals ϕ_j. For bound electrons Λ_j's will be different from o i.e., a certain amount of migration will take place even for bound electrons. (In fact it must be supposed that even the ring electrons migrate to a certain extent into the substituent; but this is negligible compared with the migration in the opposite direction. The additional space made available for the movement of electrons of the ring by the substituent is negligible compared with the space made available for the movement of the electrons

of the substituent by the ring.) But it is reasonable to presume that the migration of CH_3 electrons into the ring in $C_6H_5CH_3$ will be very small. For the other molecules considered, there will be greater degree of migration than in $C_6H_5CH_3$ connected with the fact that there are unbound electrons in these other molecules. This feature may account for the increasing divergence between the calculated and observed shifts in the substituents F, OH, NH_2, CH_3 whereas in CH_3 actually the inductive effect predominates.

It appears, therefore, that the inductive effect has also to be considered in accounting for the observed shifts especially in compounds involving migration of only bound electrons.

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