256. Hypsochromic Shifts in Methylated Hydrocarbons.

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Hypsochromic shifts produced by methyl substitution in certain unsaturated hydrocarbons are interpreted in terms of simple molecular orbital (M.O.) theory. It is shown that such shifts can only occur if one or more odd-membered rings are present, in general agreement with observation. The magnitudes of these effects calculated by second-order perturbation theory are in good agreement with those obtained by the longer procedure of solving the secular equations.

The introduction of an alkyl group into a non-alternant hydrocarbon (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39) brings about, in some cases, a shift in the longest wave-length of absorption towards the violet. It seems worth while to attempt an interpretation of this effect in terms of simple molecular orbital (M.O.) theory because, in spite of objections, this theory has had successful applications in the field of molecular spectra. We shall consider separately the inductive and hyperconjugative effects of a methyl group, and shall apply our results specifically to the molecules azulene and fulvene.

In the ground state of a molecule, the electrons occupy the bonding orbitals in pairs, and it is usual to assume that excited states are obtained by promoting electrons from the bonding orbitals into the antibonding orbitals. The first excited state is obtained when an electron is transferred from the highest bonding orbital to the lowest antibonding orbital ($N \longrightarrow V_1$ transition, in Mulliken and Rieke's notation), and it is assumed that the longest wave-length of absorption is determined by the change in energy involved in this process. Hence a change in the nature of the molecule causing a decrease in the separation of these levels will be marked by a bathochromic shift, and a change causing an increase by a hypsochromic shift.

The introduction of an alkyl group into a hydrocarbon does in fact bring about a shift in the wave-length of maximum absorption, as is well known; and, in general, (1) the shift in the case of alternant hydrocarbons is invariably a bathochromic one, but (2) with non-alternant hydrocarbons, it may be either bathochromic or hypsochromic.

The first generalisation has been accounted for in a theorem by Dewar (*J.*, 1950, 2329), who, however, ignores the inductive effect of the entering group. As regards non-alternant hydrocarbons, Pullman has shown that hypsochromic shifts are to be expected in certain cases on the basis of simple M.O. theory, and need not necessarily be attributed to steric interference. Pullman, Mayot, and Berthier (*J. Chem. Phys.*, 1950, **18**, 257) solved the secular equations for all the methylated azulenes, and compared the energies of the $N \longrightarrow V_1$ transitions in these molecules with the transition energy for azulene itself. Their method is, however, rather laborious, and is of no general illustrative value. Instead, a method is available whereby the inductive and hyperconjugation effects of the entering alkyl group may be considered separately, and the separate effects added : not only does this method lead to qualitative agreement with observation, but it also illustrates the origin of the observed hypsochromic shifts.

The Inductive Effect.—When a boundary hydrogen atom is replaced by a methyl group, the Coulomb integral of the methylated carbon atom is altered in magnitude. This perturbation will be referred to as the inductive effect. It will bring about a shift in all the orbital energies of the molecule, the energy of the *i*th M.O. being changed from ε_i to ε_i'. The relation between these two quantities can be expressed as a Taylor series involving $\delta\alpha_r$, the change in the Coulomb integral of the methylated atom, *viz.*

$$\varepsilon_i' = \varepsilon_i + \frac{\partial \varepsilon_i}{\partial \alpha_r} \cdot \delta\alpha_r + \tfrac{1}{2}\frac{\partial^2 \varepsilon_i}{\partial \alpha_r^2}(\delta\alpha_r)^2 + \dots \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Using the well-known relationships

$$\frac{\partial \varepsilon_i}{\partial \alpha_r} = c_{ir}^2 ; \quad \frac{\partial^2 \varepsilon_i}{\partial \alpha_r^2} = 2 \sum_{j(\neq i)} \frac{c_{ir}^2\, c_{jr}^2}{\varepsilon_i - \varepsilon_j}$$

(Coulson and Longuet-Higgins, *loc. cit*), where c_{ir} denotes the atomic orbital coefficient of the rth atom in the ith M.O. and neglecting terms higher than $(\delta\alpha_r)^2$, we have

$$\varepsilon_i' = \varepsilon_i + c_{ir}^2\delta\alpha_r + \sum_{j(\neq i)} \frac{c_{ir}^2\ c_{jr}^2}{\varepsilon_i - \varepsilon_j}(\delta\alpha_r)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence, if the suffixes a and b refer respectively to the highest bonding M.O. and the lowest antibonding M.O. of the unperturbed hydrocarbon, it readily follows that the net change in energy of the $N \longrightarrow V_1$ transition due to the inductive effect of the alkyl group is, by equation (2),

$$(\Delta\varepsilon_{ab})_{\text{inductive}} \equiv (\varepsilon_b' - \varepsilon_a') - (\varepsilon_b - \varepsilon_a) = (\varepsilon_b' - \varepsilon_b) - (\varepsilon_a' - \varepsilon_a)$$

$$= (c^2_{br} - c^2_{ar})\ \delta\alpha_r + \left(\sum_{j(\neq b)} \frac{c_{br}^2\ c_{jr}^2}{\varepsilon_b - \varepsilon_j} - \sum_{j(\neq a)} \frac{c_{ar}^2\ c_{jr}^2}{\varepsilon_a - \varepsilon_j}\right)(\delta\alpha_r)^2 \quad . \quad . \quad (3)$$

The Hyperconjugation Effect.—Regarding the molecule and the methyl group as two separate conjugated systems, one may consider how the orbitals of the two systems will change when they are joined, and the consequent change in the energy of the $N \longrightarrow V_1$ transition. If this hyperconjugation effect is small, it is legitimate to regard the orbitals ψ_a' and ψ_b' of the linked system as perturbed forms of the corresponding orbitals ψ_a and ψ_b in the original hydrocarbon. As before, let r be the methylated carbon atom in the hydrocarbon R, and let s be the carbon atom of the methyl group S. If β_{rs} is the resonance integral of the resulting bond, then the energy of the ith orbital changes from ε_i to ε_i', where

$$\varepsilon_i' = \varepsilon_i + \frac{\partial\varepsilon_i}{\partial\beta_{rs}} \cdot \beta_{rs} + \tfrac{1}{2}\frac{\partial^2\varepsilon_i}{\partial\beta_{rs}^2} \cdot \beta_{rs}^2 + \ldots . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now the second term on the right is a first-order perturbation term, and may be written as $\int\psi_i H'\psi_i$, where H' is the perturbation of the Hamiltonian brought about by hyperconjugation. An integral of the form $\int\psi_i H'\psi_k$ is zero unless i refers to R and k to S, or *vice versa*. This is because the only non-vanishing element of the type $\int\phi_p H'\phi_q$ (where the ϕ's denote atomic orbitals of atoms p and q respectively) is $\int\phi_r H'\phi_s = \beta_{rs}$. Therefore if i refers to a M.O. of R, the third term on the right of (4), which is a second-order perturbtion term, may be written as

$$\tfrac{1}{2}\frac{\partial^2\varepsilon_i}{\partial\beta_{rs}^2} \cdot \beta_{rs}^2 = \sum_{k(\neq i)} \frac{(\int\psi_i H'\psi_k)^2}{\varepsilon_i - \varepsilon_k} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the summation being taken over the M.O.s of S alone. Employing expansions of the type $\psi_i = \sum_p c_{ip}\phi_p$, and using the fact that $\int\phi_r H'\phi_s$ is the only non-vanishing element of its type, we can convert (5) into

$$\tfrac{1}{2}\frac{\partial^2\varepsilon_i}{\partial\beta_{rs}^2} \cdot \beta_{rs}^2 = \sum_{k(\neq i)} \frac{c_{ir}^2\ c_{ks}^2}{\varepsilon_i - \varepsilon_k} \cdot \beta_{rs}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Hence, from equation (4),

$$\varepsilon_i' = \varepsilon_i + \sum_{k(\neq i)} \frac{c_{ir}^2\ c_{ks}^2}{\varepsilon_i - \varepsilon_k} \cdot \beta_{rs}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

so that

$$(\Delta\varepsilon_{ab})_{\text{hyperconjugation}} = \beta_{rs}^2\left(\sum_{k(\neq b)} \frac{c_{br}^2\ c_{ks}^2}{\varepsilon_b - \varepsilon_k} - \sum_{k(\neq a)} \frac{c_{ar}^2\ c_{ks}^2}{\varepsilon_a - \varepsilon_k}\right) \quad . \quad . \quad . \quad (8)$$

where $(\Delta\varepsilon_{ab})_{\text{hyperconjugation}}$ is defined in a similar way to $(\Delta\varepsilon_{ab})_{\text{inductive}}$.

Combination of Effects.—It can be seen on examination that the first cross term between the inductive and hyperconjugation effects, namely, $\dfrac{\partial^2\varepsilon_i}{\partial\alpha_r\partial\beta_{rs}} \cdot \delta\alpha_r \cdot \beta_{rs}$, is zero, and hence the procedure of merely adding the separate effects is justified in this approximation. We conclude, therefore, that the total second-order change in the energy of the $N \longrightarrow V_1$ transition is given by

$$(\Delta\varepsilon_{ab})_{\text{total}} = (\Delta\varepsilon_{ab})_{\text{inductive}} + (\Delta\varepsilon_{ab})_{\text{hyperconjugation}}$$

$$= (c_{br}^2 - c_{ar}^2)\delta\alpha_r + \left(\sum_{j(\neq b)} \frac{c_{br}^2\, c_{jr}^2}{\varepsilon_b - \varepsilon_j} - \sum_{j(\neq a)} \frac{c_{ar}^2\, c_{jr}^2}{\varepsilon_a - \varepsilon_j}\right)(\delta\alpha_r)^2$$

$$+ \left(\sum_{k(\neq b)} \frac{c_{br}^2\, c_{ks}^2}{\varepsilon_b - \varepsilon_k} - \sum_{k(\neq a)} \frac{c_{ar}^2\, c_{ks}^2}{\varepsilon_a - \varepsilon_k}\right)\beta_{rs}^2 \quad . \quad . \quad . \quad (9)$$

The two generalisations cited earlier may now be explained in terms of equation (9), it being borne in mind that the term in $(\delta\alpha_r)^2$ is small compared with the other two terms. For alternant hydrocarbons, $c_{ar}^2 = c_{br}^2$ (Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193), so the inductive term in $\delta\alpha_r$ vanishes, and the hyperconjugation term governs the situation. It is now required to show that this hyperconjugation term is of necessity negative.

According to Mulliken *et al.* (*J. Amer. Chem. Soc.*, 1941, **63**, 41), a conjugating methyl group may be regarded as analogous to $-C{\equiv}N$, and written as $-C{\equiv}H_3$. After allowance for the fact that the Coulomb integral of the H_3 group is less than that of the C atom, solution of the secular equation gives two M.O., ψ_1 and ψ_2, with energies ε_1 and ε_2 where $\varepsilon_1 < -\varepsilon_2$. The hyperconjugation term of (9) is in this case seen to be given by

$$\beta_{rs}^2\, c_{ar}^2 \left\{ c^2_{1s}\left(\frac{1}{\varepsilon_b - \varepsilon_1} - \frac{1}{\varepsilon_a - \varepsilon_1}\right) + c_{2s}^2\left(\frac{1}{\varepsilon_b - \varepsilon_2} - \frac{1}{\varepsilon_a - \varepsilon_2}\right)\right\} \quad . \quad (10)$$

where c_{1s}, c_{2s} are the atomic orbital (A.O.) coefficients for the carbon atom in ψ_1 and ψ_2. If

$$\varepsilon_1 < \varepsilon_a < 0 < \varepsilon_b < \varepsilon_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10a)$$

this expression will always be negative. Now for $C{\equiv}H_3$, ε_1 and $-\varepsilon_2$ are both approximately equal to 2β. For unsaturated hydrocarbons, on the other hand, ε_a and $-\varepsilon_b$ are fractions of β, so that the above inequalities hold, and $(\Delta\varepsilon_{ab})_{\text{hyperconjugation}} < 0$. In alternant hydrocarbons, therefore, the shift is always bathochromic.

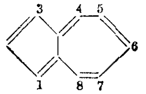
For non-alternant hydrocarbons, the hyperconjugation term may be written

$$(\Delta\varepsilon_{ab})_{\text{hyperconjugation}} = \beta_{rs}^2 \left\{ c_{br}^2 \left(\frac{c_{1s}^2}{\varepsilon_b - \varepsilon_1} + \frac{c_{2s}^2}{\varepsilon_b - \varepsilon_2}\right) - c_{ar}^2 \left(\frac{c_{1s}^2}{\varepsilon_a - \varepsilon_1} + \frac{c_{2s}^2}{\varepsilon_a - \varepsilon_2}\right)\right\} \quad . \quad (11)$$

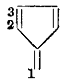
By assuming $\varepsilon_1 = -\varepsilon_2$, and the inequalities (10*a*), it is seen that $(\Delta\varepsilon_{ab})_{\text{hyperconjugation}} < 0$ in all cases, and this is the condition for a bathochromic shift. [The assumption $\varepsilon_1 = -\varepsilon_2$ implies equal Coulomb integrals for the C and H_3 orbitals of the methyl group; this assumption, though perhaps not exactly correct (see above), is almost certainly adequate for determining the sign of $(\Delta\varepsilon_{ab})_{\text{hyperconjugation}}$.]

The essential difference, according to this treatment, between alternant and non-alternant hydrocarbons is that in the latter, the term in $\delta\alpha_r$ does not vanish. Indeed, if $c_{br}^2 > c_{ar}^2$, this term will by itself tend to produce a hypsochromic shift, since, for alkyl substitution, $\delta\alpha_r$ is positive. Hence, alkyl substitution in non-alternant hydrocarbons may produce either bathochromic or hypsochromic shifts—perhaps shifts of opposite sense by substitution at different positions—according to the geometry of the molecule. If $c_{br}^2 < c_{ar}^2$ it can be seen at once that a hypsochromic shift will not be produced by substitution at atom r.

Application to Methylated Azulene and Fulvene.—As has already been mentioned, theoretical work by Pullman *et al.* on azulene and its methylated derivatives has led in all cases to a qualitative agreement with the spectral shift observed on methylation. The approximate method described above has been applied to the same molecules, the value of $\delta\alpha_r$ being taken to be $-0{\cdot}1\beta$, that of β_{rs} to be $0{\cdot}7\beta$, the resonance integral of $C{\equiv}H_3$ to be 2β, and the Coulomb integral of H_3 to be $\alpha - 0{\cdot}2\beta$, where β is the resonance integral of the carbon–carbon bond, and α is the Coulomb integral of the carbon atom, all these values being those employed by Pullman. The correction to the resonance integral of the binuclear bond, introduced in Pullman's work, has not been applied here. The calculated changes in energy of the $N \longrightarrow V_1$ transitions are as given in the table, the atoms being numbered as in (I), and they are seen, on the whole, to compare well with those obtained



(I)



(II)

by exact solution of the secular equations. What is more important, the results agree qualitatively with experimental observation, predicting a bathochomic shift at positions 3 and 5, and a hypsochromic one at positions 2, 4, and 6. For fulvene, numbered as in (II), application of the approximate method leads to the prediction of a hypsochromic shift on substitution at position 1 in accordance with the predictions of Pullman *et al.* (*J. Chem. Physics*, 1950, **18**, 257).

	$N \longrightarrow V_1$ change (in β units) calculated	
Position of Me group	approximately	by soln. of secular eqns.
2	0·0056	0·0080
3	−0·0547	−0·0525
4	0·0088	0·0075
5	−0·0156	−0·0234
6	0·0148	0·0172

Extension to Dimethyl Derivatives.—Šorm and Knessel (*Coll. Czech. Chem. Comm.*, 1949, **14**, 201) have carried out studies on the 2 : 6- and 4 : 6-dimethyl derivatives of azulene, and have measured the hypsochromic shifts produced in the $N \longrightarrow V_1$ peak by dimethyl substitution. In the following table, these observed values are compared with those obtained by calculation, the effects of methyl substitution being assumed to be additive. The experimental data for the 2-, 4-, and 6-monomethylazulenes are taken from Plattner and Heilbronner (*Helv. Chim. Acta*, 1947, **30**, 910).

Hypsochromic shifts (mμ) *in* N $\longrightarrow$ V_1 *peak in methyl-substituted azulenes.*

2-Me, obs.	6-Me, obs.	2 : 6-Me$_2$, calc.	2 : 6-Me$_2$, obs.	4-Me, obs.	6-Me, obs.	4 : 6-Me$_2$, calc.	4 : 6-Me$_2$, obs.
−21	−16	−37	−37	−17	−16	−33	−35

The observed additivity is interpreted as follows. Since the inductive effect, as we have represented it, is a first-order perturbation at the position of substitution, this effect will be additive for two or more substituents. Accordingly, we need only consider the effect of hyperconjugation. If perturbation of the *i*th orbital is brought about by substitution of two methyl groups in the molecule, equation (4) becomes

$$\varepsilon_i' = \varepsilon_i + \frac{\partial\varepsilon_i}{\partial\beta_1}\cdot\beta_1 + \frac{\partial\varepsilon_i}{\partial\beta_2}\cdot\beta_2 + \frac{\partial^2\varepsilon_i}{\partial\beta_1{}^2}(\beta_1)^2 + \frac{\partial^2\varepsilon_i}{\partial\beta_2{}^2}(\beta_2)^2 + \frac{\partial^2\varepsilon_i}{\partial\beta_1\partial\beta_2}\cdot\beta_1\beta_2 + \dots \qquad (12)$$

where the suffixes 1 and 2 refer to the two groups. It is seen that additivity of the hyperconjugation effect is conditioned by whether or not the cross term $\frac{\partial^2\varepsilon_i}{\partial\beta_1\partial\beta_2}\cdot\beta_1\beta_2$ vanishes.

The fact that the cross-term does vanish becomes apparent if the expansion is written in the form

$$\varepsilon_i' = \varepsilon_i + \int\psi_i H'\psi_i + \sum_{(\neq i)} \frac{(\int\psi_i H'\psi_j)^2}{\varepsilon_i - \varepsilon_j} + \dots \qquad (13)$$

Here ψ_i is an orbital of the unsubstituted system, and ψ_j is an orbital of one or other of the entering methyl groups. Hence each term in the sum must contain either β_1 or β_2, but not both : the cross term is therefore zero.

Reduction Potentials.—According to Maccoll (*Nature*, 1949, **162**, 178), the heat of reduction ΔH of a conjugated molecule may be taken as the energy required to place one or two electrons in the lowest unoccupied orbital, which is, in the ground state, the lowest antibonding orbital. If this is correct, any change in the energy of this orbital should be reflected in a change in the value of ΔH. From the calculations described above, it is found that the A.O. coefficient c_{ar} of the highest bonding orbital in azulene is zero at positions 2 and 6, and that this coefficient is zero at position 1 of fulvene. Thus, by equation (9), any change in $N \longrightarrow V_1$ energy brought about by methyl substitution at these positions is due to displacement of the lowest antibonding orbital. Hence the hypsochromic shifts caused by substitution of various groups at these positions would be expected to run parallel to the changes brought about in the heat of reduction.

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