

FREE-ELECTRON THEORY OF SUBSTITUENT EFFECTS ON MOLECULAR ORBITAL COEFFICIENTS

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Abstract

Rules for substituent effects on MO coefficients are developed by perturbational free-electron theory. The π -MOs of substituted polyenes are regarded as waves shifted toward an electronegative atom in the conjugated system or shifted away from an electron-donating group. The concepts are extended to substituted benzenes to show the relative magnitudes of the HOMO coefficients at ortho/para and meta carbons.

1. Introduction

The rules for substituent effects on MO coefficients were presented by Houk [1] accompanying an explanation of the regioselectivity of cycloaddition reactions. For these rules, as well as the rules pertaining to substituted benzenes, Fleming [2] proposed a concept based on the following assumptions: The MOs of the π -system with an electron-withdrawing and conjugative substituent (Z-substituent, e.g. formyl, carboxyl, cyano) can be regarded as those with a pure conjugative substituent (C-substituent, e.g. vinyl, phenyl) incorporated with some contribution of the MOs of the corresponding cation in which a CH_2^+ is in place of the Z-substituent. The MOs of the π -system with a π -electron-donating substituent (X-substituent, e.g. methoxyl, dimethylamino, methyl) can be regarded as those of the unsubstituted system incorporated with some contribution of the MOs of the corresponding anion in which a CH_2^- is in place of the X-substituent. However, the concept does not have a theoretical basis and fails in the case of the LUMO of 1-X-substituted butadiene.

In principle, these rules should be deduced based on perturbation theory. In this work, the π -MOs of polyenes are regarded as sine waves in the model of a free-electron in a one-dimensional box, and the substituent effect will be regarded as a perturbation distorting the waves.

2. Theory

We assume an increase of electronegativity of the last atom, i.e. the n th atom of a polyene with n conjugated carbon atoms, just as a substitution of an isoelectronic group, NH or O, for the terminal CH_2 group. In the framework of HMO theory, the corresponding n th diagonal element of the HMO matrix should be increased by a positive value, which is denoted by P and regarded as a perturbation. The element of the perturbation matrix between MOs i and j is thus

$$H'_{ij} = P c_{ni} c_{nj}, \quad (1)$$

where c_{ni} is the coefficient of the n th AO in the i th MO.

It is well known that for polyenes the coefficients are given by

$$c_{\mu i} = (2/l)^{1/2} \sin(i\pi\mu/l), \quad (2)$$

where

$$l = n + 1. \quad (3)$$

It follows that

$$H'_{ij} = P(2/l) \sin(i\pi n/l) \sin(j\pi n/l). \quad (4)$$

According to perturbation theory, the perturbed i th MO up to the first-order term is

$$\psi_i = \psi_i^{(0)} + \sum_j H'_{ij} \psi_j^{(0)} / (\epsilon_i^{(0)} - \epsilon_j^{(0)}). \quad (5)$$

Substituting eq. (4) into eq. (5), we have

$$\psi_i = \psi_i^{(0)} + P(2/l) \sin(i\pi n/l) \sum_j \sin(j\pi n/l) \psi_j^{(0)} / (\epsilon_i^{(0)} - \epsilon_j^{(0)}). \quad (6)$$

In principle, the rules of the deviation of coefficients can be deduced from eq. (6). However, it is very difficult to obtain simple and general rules of deviation from eq. (6). Since the coefficients of polyenes can be generalized by the sine waves following from free-electron theory, we will try to generalize the rules in terms of distortion of the wave.

As is well known, the unperturbed wave functions of a particle-in-box are

$$\psi_i^{(0)} = (2/l)^{1/2} \sin(i\pi x/l), \quad i = 1, 2, \dots, \quad (7)$$

where l is the length of the one-dimensional box, and x is the coordinate along the box. The corresponding MO energies are

$$\epsilon_i^{(0)} = i^2 \pi^2 / 2l^2. \quad (8)$$

For a polyene with n conjugated carbon atoms, the length of the box should be $n + 1$ times a CC bond length. Regarding a CC bond length as the unit of length, we have $l = n + 1$, consistent with eq. (3). The positions of the nuclei are assumed to be at the points dividing the box into l equal parts, and the ψ value at a dividing point is just the same as the corresponding HMO coefficient.

Assuming a perturbation leading to a decrease of the potential energy around the last atom, where $x = n$,

$$\hat{H}' = -B, \quad \text{if } x_1 < x < x_2, \quad \text{else } \hat{H}' = 0, \quad (9)$$

we have the perturbation matrix element between MOs i and j

$$H'_{ij} = -B(2/l) \int_{x_1}^{x_2} \sin(i\pi x/l) \sin(j\pi x/l) dx. \quad (10)$$

For simplicity, assuming the interval between x_1 and x_2 small enough, we can simplify the above equation to

$$H'_{ij} = -C(2/l) \sin(i\pi n/l) \sin(j\pi n/l), \quad (11)$$

where $C = B(x_2 - x_1)$. The perturbed MO is thus obtained by substituting eq. (11) into eq. (5). Omitting the normalization factor $(2/l)$, we have the unnormalized wave function

$$\psi_i = \sin(i\pi x/l) + D \sin(i\pi n/l) \sum_j' \sin(j\pi n/l) \sin(j\pi x/l) / (j^2 - i^2), \quad (12)$$

where $D = 4Cl/\pi^2$. The consistency of eqs. (11) and (12) with eqs. (4) and (6) shows the relationship between the free-electron model and the above-mentioned HMO model. The rate of deviation of the coefficient versus the extent of the perturbation can be explicitly expressed by

$$(\partial \psi / \partial D)_x = \sin(i\pi n/l) \sum_j' \sin(j\pi n/l) \sin(j\pi x/l) / (j^2 - i^2), \quad (13)$$

where x represents the position of the atom where the coefficient is under consideration.

It is just as difficult as above to obtain simple and general rules of deviation of coefficients due to the perturbation directly from eq. (13). Hence, we will express the rules in terms of the distortion of the wave along the one-dimensional box.

The distortion can be represented by the shift of the nodes of the wave. The shift direction of the wave nodes with increasing D depends on the sign of the derivative $(\partial x / \partial D)_\psi$ at the nodes, which can be separated into

$$(\partial x / \partial D)_\psi = -(\partial \psi / \partial D)_x / (\partial \psi / \partial x)_D, \quad (14)$$

where the derivative in the denominator corresponds to $D = 0$, i.e. the unperturbed wave function. Thus,

$$(\partial\psi/\partial x)_D = d\psi^{(0)}/dx = (i\pi/l) \cos(i\pi x/l). \quad (15)$$

At the nodes of $\psi^{(0)}$, $\sin(i\pi x/l) = 0$, the angle $i\pi x/l$ should be an integral multiple of π , i.e. $k\pi$, where k is an integer,

$$k = ix/l, \quad 0 < k < i. \quad (16)$$

Thus,

$$(\partial\psi/\partial x)_D > 0 \quad \text{if } k \text{ is even,} \quad \text{else } (\partial\psi/\partial x)_D < 0. \quad (17)$$

The sign of $(\partial\psi/\partial D)_x$ depends on the most significant interaction from the nearest MOs with $j = i \pm 1$. It can be proven that (cf. the appendix) these terms are negative if k is even, else positive. As a result, the sign of $(\partial\psi/\partial D)_x$ is always opposite to that of $(\partial\psi/\partial x)_D$, and $(\partial x/\partial D)_\psi$ in eq. (14) is always positive. It is thus concluded that the wave nodes will be shifted toward the atom with a positive D value, i.e. an electron-withdrawing atom, and will be shifted away from the atom with a negative D value, i.e. the terminal carbon linking it to an electron-donating substituent. Since the ψ value at both terminuses of the box should be zero, shifting the middle part of the wave results in distortion of the wave, as shown in fig. 1.

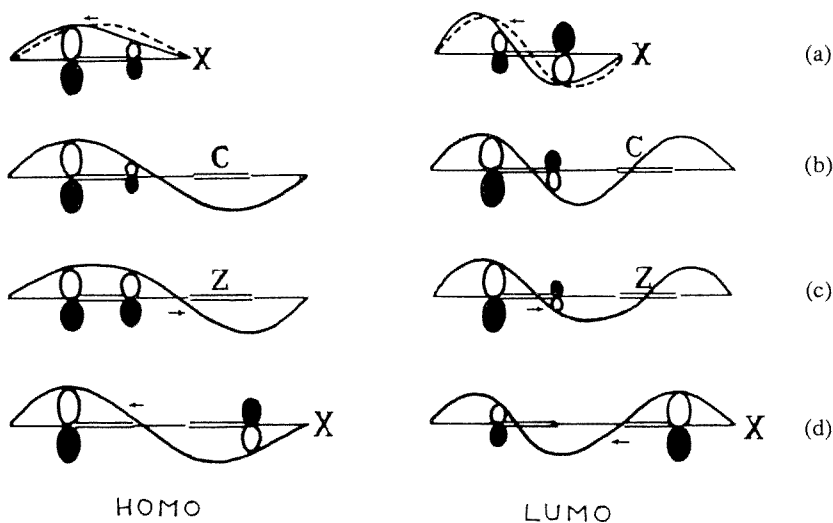


Fig. 1. Relative magnitude of terminal coefficients shown by shifts of waves (the dashed lines denote ethylene).

3. Applied examples

3.1. 1-SUBSTITUTED POLYENES

An X-substituted polyene is simulated by an unsubstituted one with a negative D value at the substituted position. Thus, an X-substituted ethylene is pictured as in fig.

1(a), in which the waves are shifted away from the substituted position to the left as compared with the waves of ethylene. The coefficient on the left-hand side (unsubstituted) atom will be greater than that on the right-hand side in the HOMO, while smaller than that on the right-hand side in the LUMO. Figure 1(d) shows the wave of X-substituted butadiene based on the left shift of the waves of butadiene shown in fig. 1(b) to realize similar changes which cannot be realized by Fleming's conception.

For a C-substituted polyene, the waves are obtained by lengthening the box. Thus, the waves of the HOMO and the LUMO of a C-substituted ethylene are obtained by adding two units in length and one half-wave to those of ethylene. Since the half-wave in the HOMO of ethylene is longer than two units, the wave is compressed to the left (the unsubstituted terminus). On the other hand, the half-wave in the LUMO of ethylene is shorter than two units, so the wave is extended to the right. As a result, the coefficients at the substituted terminus in both HOMO and LUMO become smaller, as shown in fig. 1(b).

A Z-substituted polyene is simulated by the corresponding C-substituted polyene with a positive D value at the electron-withdrawing atom. Thus, acrolein is simulated by butadiene with a positive D value at the fourth atom, shown in fig. 1(c). The waves are shifted to the right as compared with the corresponding C-substituted ethylene shown in fig. 1(b). The coefficient on the substituted (right) atom becomes larger in the HOMO and becomes smaller in the LUMO.

In the above cases, the relative magnitudes of the coefficients predicted by the wave shift are all in agreement with Houk's empirical rules summarized from the results of various MO methods.

3.2. 2-SUBSTITUTED AND POLYSUBSTITUTED BUTADIENES

A substituent on C^2 of butadiene affects mainly the fragment of C^1C^2 , as pointed out by Fleming [2]. The relative magnitude of the coefficient on C^1 with respect to that on C^2 is thus realized by the same concept as in the case of substituted ethylenes. Thus, the LUMO coefficient on C^1 will be smaller than that on C^4 in 2-X-substituted butadienes, while the HOMO and LUMO coefficients on C^1 will be larger in other cases (cf. figs. 1(a)–(c)).

As for polysubstituted butadienes, the relative magnitude of coefficients on both terminuses can be readily predicted if the effects of the substituents are in the same direction. Thus, in 1-methyl-4-formylbutadiene, the waves are shifted to the right, so the HOMO coefficient on C^1 will be smaller, while the LUMO coefficient on C^1 will be larger. The same feature will exist in the case of 1,3-dimethylbutadiene, since both methyl groups drive the waves toward C^4 .

3.3. HETERO-POLYENES

Acrolein serves as a typical example of a hetero-polyene. Since the waves are shifted by the oxygen toward itself, the HOMO coefficient on the oxygen will be larger

than on the terminal carbon, while the LUMO coefficient on the oxygen will be smaller (cf. fig. 1(c)).

The above cases are related to cycloaddition chemistry for predicting regioselectivity, as summarized in the book by Fleming [2].

3.4. RING SYSTEMS

The concepts can be extended to ring systems. The waves on a ring are regarded as propagating (strictly speaking, standing) on both sides of the ring (the upper and lower sides in fig. 2). If the two sides are combined into one, the π -system can also be simulated by the free-electron model.

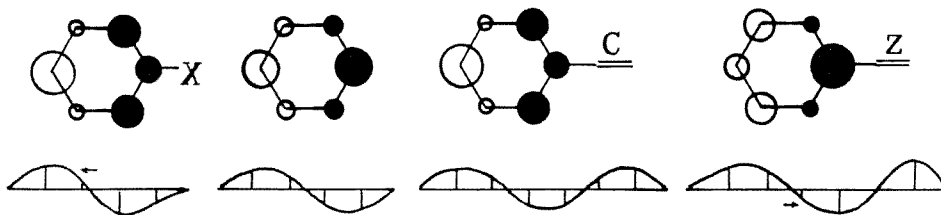


Fig. 2. Substituent effect on one of the HOMOs in benzene.

There are degenerate HOMOs in benzene. One of the HOMOs is antisymmetrical with respect to the plane perpendicular to the carbon plane and contains C^1 and C^4 . The coefficients on C^1 and C^4 are zero, and the wave will not be affected by any substituent on C^1 . Hence, only the other HOMO is considered.

The waves of an X-substituted benzene are regarded as resulting from the waves of benzene shifted away from the substituted terminus. The ortho/para coefficients of the HOMO are thus increased. This is in agreement with the fact that electrophilic attacks are preferential at the ortho/para carbon of an X-substituted benzene. A C-substituent lengthens the box and gives the same effect on the HOMO as an X-substituent does. For a Z-substituted benzene, the waves are obtained by shifting the waves of a C-substituted benzene toward the substituent. The change of HOMO is in the opposite direction against that given by a C-substituent. When the electron-withdrawing effect of the Z-substituent is large enough, the meta coefficients of the HOMO will become greater than the ortho ones, favoring electrophilic attacks at the meta carbons. These features are shown in fig. 2 with exaggeration.

Heteroatoms on the ring are similar to those on polyenes. Thus, the nitrogen in pyridine shifts the wave of benzene toward itself, the result being the same as Z-substituted benzene on the right-hand side of fig. 2.

Appendix

A proof of the rule of the sign of the terms with $i = j \pm 1$ in eq. (13) is provided here.

- (1) The sign of $\sin(i\pi n/l)\sin(j\pi n/l)$. The angle in the first factor, i.e. $i\pi n/l$, is less than $i\pi$ by an angle $i\pi/l$ less than π (note that $n = l - 1$ and $i < l$). Similarly, $j\pi n/l$ is less than $j\pi$ by an angle less than π . Since $j = i \pm 1$, the terminate sides of the angles $i\pi$ and $j\pi$ should be in the opposite directions of the abscissa. Thus, the terminate sides of the angles $i\pi n/l$ and $j\pi n/l$ should be in different half planes separated by the abscissa. As a result, $\sin(i\pi n/l)$ and $\sin(j\pi n/l)$ should have opposite signs, and their product should be negative.
- (2) The sign of $\sin(j\pi k/i)/(j^2 - i^2)$. As the angle $j\pi k/i = k\pi \pm k\pi/i$, the difference between $j\pi k/i$ and $k\pi$ should be less than π (note that $k < i$). In the case where k is even, the terminate side of $k\pi$ is in the positive direction of the abscissa, and the terminate side of $j\pi k/i$ is in the upper half plane if $j = i + 1$, while it is in the lower half plane if $j = i - 1$. As a result, the sign of the quotient $\sin(j\pi k/i)/(j^2 - i^2)$ is positive in the case where k is even, while it is negative in the case where k is odd.

Therefore, the terms with $j = i \pm 1$ should be negative if k is even; otherwise positive.

Acknowledgement

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References

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