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The electronic structure of conjugated systems

II. Unsaturated hydrocarbons and their hetero-derivatives

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The theory of Part I (Coulson & Longuet-Higgins 1947) is applied to hydrocarbons and their hetero-derivatives. An equation is given relating differences in activation energy to electron densities and atom polarizabilities (in the sense of Part I) for a heterolytic reaction at different positions in a conjugated system. The equations of Part I are then applied to hydrocarbons containing no odd-membered unsaturated rings. It has previously been shown that in such hydrocarbons all the electron densities are unity, and it is here proved that when one coulomb integral is altered slightly, the electron densities are alternately increased and decreased throughout the molecule. This fact is shown to provide a theoretical basis for the experimental law of alternating polarity in conjugated systems containing a hetero-atom.

INTRODUCTION

In the first paper of this series (Coulson & Longuet-Higgins 1947) we showed how it was possible to calculate electron densities, bond orders and mutual polarizabilities in any conjugated system. In the present paper we shall use those results

to interpret the chemical behaviour of the more simple types of conjugated system, and to predict how the reactivity of different positions in more complex molecules is altered when an atom is changed.

ELECTRONIC STRUCTURE AND CHEMICAL REACTIVITY

Let us begin by considering the energy changes which occur when a charged reagent is brought up to a reactive position in a conjugated system. We may think of this energy change as arising from various causes, including (a) polarization of non-bonding electrons and σ -electrons, (b) interpenetration of electronic shells in space, i.e. steric effects, and (c) changes in the energy of the mobile electrons. It is reasonable to suppose that the last factor principally determines the differences in activation energy for a given reaction at different positions in a conjugated system, when structural and steric conditions are nearly the same.

Now the energy \mathcal{E} of the mobile electrons is a function only of the resonance integrals β_{rs} of the bonds and the coulomb terms α_r of the atoms. Therefore when we are considering the approach of a reagent to position r , say, we should expect the change in \mathcal{E} to arise mainly from the induced change in α_r , the coulomb term for that atom. We may express this dependence by expanding $\delta\mathcal{E}$ as a Taylor's series in $\delta\alpha_r$, thus:

$$\delta\mathcal{E} = \frac{\partial\mathcal{E}}{\partial\alpha_r}\delta\alpha_r + \frac{1}{2}\frac{\partial^2\mathcal{E}}{\partial\alpha_r^2}\delta\alpha_r^2 + \dots \quad (1)$$

But by equations (24) and (46) of Part I

$$\frac{\partial\mathcal{E}}{\partial\alpha_r} = q_r, \quad \frac{\partial^2\mathcal{E}}{\partial\alpha_r^2} = \pi_{r,r}. \quad (2)$$

Therefore for a given type of reaction we are correlating the activation energies at different positions primarily with the electron densities q_r and secondarily with the self-polarizabilities $\pi_{r,r}$ of those positions.

At this point we must distinguish two types of reagent. These are familiar to organic chemists as cationoid and anionoid reagents. One difference is that the former bear a net positive charge at the attacking point, and the latter a net negative charge. We should therefore expect the approach of a cationoid reagent to lead to a decrease in α_r , and that of an anionoid reagent to an increase in α_r . Now the larger the value of \mathcal{E} in the transition state the larger the activation energy. We deduce that cationoid reactions will be favoured by high values of q_r , and anionoid reactions by low values of q_r . (This agrees, of course, with the qualitative resonance picture, which is explained fully in Wheland (1944).)

These expectations have been entirely confirmed by calculations for a number of familiar molecules, mostly of the hetero-aromatic type, such as pyridine and indole; the calculated electron densities are found to agree very well with the above generalization (Wheland & Pauling 1935; Longuet-Higgins & Coulson 1947). However,

there are many hydrocarbons, as we shall see later, in which the values of q_r are the same at a number of positions. In such cases we must fall back on the term $\frac{1}{2} \frac{\partial^2 \mathcal{E}}{\partial \alpha_r^2} \delta \alpha_r^2$ in equation (1) for information about the relative activation energies of a reaction at these positions. Now whatever the value of $\delta \alpha_r$, $\delta \alpha_r^2$ is positive, and $\pi_{r,r}$ is necessarily negative (by Part I, equation 71). Therefore whether we are considering an anionoid or a cationoid reaction, we should expect the reaction to go more easily the larger the numerical value of $\pi_{r,r}$. And in fact Wheland & Pauling (1935) showed that in naphthalene the greater reactivity of the α -positions towards both cationoid and anionoid reagents was paralleled by the greater self-polarizability of the α -positions, the electron densities being equal at all positions. We shall discuss other examples later in this paper.

(We shall not consider homolytic reactions here, i.e. reactions involving free radicals, because the formulae of the present theory do not all hold for molecules containing odd numbers of electrons.)

THE LAW OF ALTERNATING POLARITY

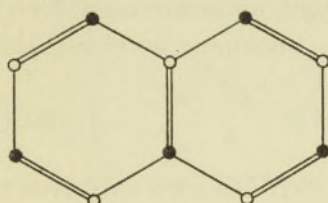
Having established a relation between calculated electron densities and observed chemical reactivities, we may now inquire whether the theory enables us to make any general predictions about the effect of structural changes on electron densities and hence on chemical behaviour. In anticipating what general results to expect we must obviously be guided by the experimental evidence; and a very great deal of this is summed up in the *law of alternating polarity*, which may be stated in the following form: in a conjugated molecule containing one hetero-atom or substituent, the atoms are alternately more and less susceptible to anionoid or cationoid reagents as we proceed through the molecule. This result is so familiar as to be almost commonplace, but it has not hitherto been given a quantitative interpretation in resonance theory.

The form in which we have stated the law makes clear at once what types of molecule we should choose for investigation. It will be no use trying to derive the law for molecules which have odd-membered rings of unsaturated atoms, if only because it is meaningless to speak of the atoms round an *odd*-membered ring as being *alternately* more and less susceptible to a given kind of reagent. Also, the substitution of more than one hetero-atom in a conjugated hydrocarbon will clearly alter the form of the law as we have stated it. To begin with, therefore, we investigate unsaturated hydrocarbons in which there are no odd-membered rings, and later we shall see how their electronic structures change when one carbon is replaced by a hetero-atom.

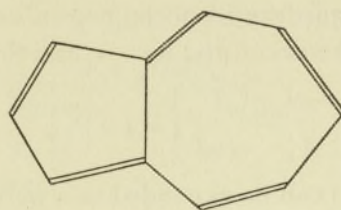
ALTERNANT HYDROCARBONS

Suppose we have a hydrocarbon in whose molecule there are no rings composed of an odd number of unsaturated carbon atoms. Then it is possible to divide the unsaturated carbon atoms into two sets in such a way that no two atoms of the same

set are joined by a bond. Therefore as we move along any chain of unsaturated bonds the atoms will belong alternately to one set and to the other. For this reason we shall refer to such a hydrocarbon as an *alternant hydrocarbon* (a.h.). Thus naphthalene is an alternant hydrocarbon (in the accompanying diagram the black circles represent atoms of one set and the white circles those of the other), whereas azulene is not. This type of molecule has been investigated by Coulson & Rushbrooke (1940). We shall restate many of their results in what follows.



naphthalene



azulene

THE SECULAR EQUATIONS

If we number all the atoms of one set from 1 to h , and all the atoms of the other set from $h+1$ to n , the secular equations will be (see Part I, equation (12)):

$$\left. \begin{aligned} -\epsilon c_r + \sum_{s=h+1}^n \beta_{rs} c_s &= 0 \quad (r = 1, 2, \dots, h), \\ -\epsilon c_r + \sum_{s=1}^h \beta_{rs} c_s &= 0 \quad (r = h+1, h+2, \dots, n). \end{aligned} \right\} \quad (3)$$

The secular determinant for an alternant hydrocarbon is therefore of the form

$$\Delta(\epsilon) = \begin{vmatrix} -\epsilon & 0 & 0 & \dots & \beta_{1,h+1} & \beta_{1,h+2} & \dots \\ 0 & -\epsilon & 0 & \dots & \beta_{2,h+1} & \beta_{2,h+2} & \dots \\ 0 & 0 & -\epsilon & \dots & \vdots & \vdots & \\ \vdots & \vdots & \vdots & & \vdots & & \\ & & & \dots & -\epsilon & & \\ \beta_{1,h+1} & \beta_{2,h+1} & \beta_{3,h+1} & \dots & -\epsilon & 0 & \dots \\ \beta_{1,h+2} & \beta_{2,h+2} & \beta_{3,h+2} & \dots & 0 & -\epsilon & \dots \\ \vdots & \vdots & \vdots & & \vdots & \vdots & \\ & & & \dots & \beta_{h,n} & & -\epsilon \end{vmatrix}$$

Here the first h rows and columns refer to the atoms of one set, and the other $n-h$ rows and columns to those of the other. For brevity we may write

$$\Delta(\epsilon) = \begin{vmatrix} -\epsilon I & A \\ \bar{A} & -\epsilon J \end{vmatrix}, \quad (4)$$

where I and J are unit matrices of orders h and $n-h$, and A, \bar{A} are the two blocks of resonance integrals β_{rs} . Although it is customary to put all the β 's equal in numerical calculations for hydrocarbons, none of our general results will depend on the equality of the β 's.

MOLECULAR ORBITALS IN AN ALTERNANT HYDROCARBON

As Coulson & Rushbrooke have shown, there is a close correspondence between the occupied and unoccupied m.o. of an alternant hydrocarbon. If we multiply the first h rows of $\Delta(\epsilon)$ by -1 , and then the last $n-h$ columns, we obtain the identity

$$\Delta(\epsilon) = \begin{vmatrix} -\epsilon I & A \\ \bar{A} & -\epsilon J \end{vmatrix} = (-)^h \begin{vmatrix} \epsilon I & -A \\ \bar{A} & -\epsilon J \end{vmatrix} = (-)^n \begin{vmatrix} \epsilon I & A \\ \bar{A} & \epsilon J \end{vmatrix} = (-)^n \Delta(-\epsilon). \quad (5)$$

Now $\Delta(\epsilon)$ can be expanded as a polynomial in ϵ ; so if n is even only even powers of ϵ occur in the expansion, whereas if n is odd only odd powers occur. Therefore if n is even the roots of $\Delta(\epsilon) = 0$ occur in equal and opposite pairs, whereas if n is odd there is also a root $\epsilon = 0$. We shall now consider these two cases separately.

n even

As we have seen, when n is even the m.o. occur in pairs with equal and opposite energies. We have supposed that there are no repeated roots of $\Delta = 0$, so no m.o. can have zero energy. If we label the m.o. energies in order from ϵ_1 to ϵ_n , so that

$$\epsilon_1 < \epsilon_2 < \dots < \epsilon_{\frac{1}{2}n} < 0 < \epsilon_{\frac{1}{2}n+1} < \dots < \epsilon_n, \quad (6)$$

it follows that

$$\epsilon_{n-j+1} = -\epsilon_j. \quad (7)$$

Now in an uncharged a.h. with n unsaturated carbons there will be n π -electrons; so in the ground state these will occupy the $\frac{1}{2}n$ lowest m.o. Therefore the requirements laid down in Part I are satisfied by even-numbered a.h., and our general theory applies to them.

Now if in the secular equations (3) we write $-\epsilon$ for ϵ throughout and $-c_r$ for c_r when r has the values $1, 2, \dots, h$, the equations are unaltered. It follows from (7) that

$$\begin{aligned} c_{r, n-j+1} &= -c_{rj} & \text{when } r &= 1, 2, \dots, h \\ &= +c_{rj} & \text{when } r &= h+1, h+2, \dots, n, \end{aligned} \quad (8)$$

i.e. that the coefficients in the $(n-j+1)$ th m.o. equal those in the j th apart from a factor -1 for all the atoms of one set.

We can infer at once that when we excite an electron from the m.o. ψ_j to the m.o. ψ_{n-j+1} the contribution of that electron to the order of any bond is reversed in sign but unaltered in magnitude. This is because any two atoms forming a bond must belong to different sets by the definition of an a.h., and therefore the product $c_{r, n-j+1} c_{s, n-j+1}$ equals $-c_{rj} c_{sj}$. An important special case is when an electron in the highest occupied m.o. $\psi_{\frac{1}{2}n}$ is excited to the lowest unoccupied m.o. $\psi_{\frac{1}{2}n+1}$. If the electron contributed to the binding between two atoms before excitation, it will be antibonding for them after excitation, and vice versa.

In Part I we defined the mutual polarizability of a pair of atoms or a pair of bonds (see Part I, equations (46) and (51)). With the aid of equations (7) and (8) we can simplify equations (64) and (67) of Part I by expressing the right-hand sides entirely in terms of quantities referring to the occupied m.o. The results are

$$\pi_{s,r} \left(= \frac{\partial q_s}{\partial \alpha_r} \right) = \pm 4 \sum_{j=1}^{1n} \sum_{k=1}^{1n} \frac{c_{rj} c_{sj} c_{rk} c_{sk}}{\epsilon_j + \epsilon_k}, \quad (9)$$

+ or - according as r and s belong to the same set or opposite sets, and

$$\pi_{rs,tu} \left(= \frac{\partial p_{rs}}{\partial \beta_{tu}} \right) = 4 \sum_{j=1}^{1n} \sum_{k=1}^{1n} \frac{(c_{rj} c_{sk} - c_{sj} c_{rk}) (c_{tj} c_{uk} - c_{uj} c_{tk})}{\epsilon_j + \epsilon_k}, \quad (10)$$

where r and t are understood to be in the same set.

n odd

As we saw, when n is odd all the m.o. of an a.h. except one occur in pairs with equal and opposite energies, the remaining one having zero energy. We may label the m.o. energies in order thus:

$$\epsilon_1 < \epsilon_2 < \dots < \epsilon_{\frac{1}{2}(n-1)} < \epsilon_{\frac{1}{2}(n+1)} = 0 < \epsilon_{\frac{1}{2}(n+3)} < \dots < \epsilon_n, \quad (11)$$

where

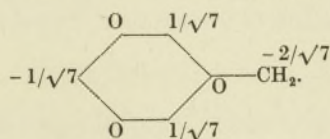
$$\epsilon_{n-j+1} = -\epsilon_j, \quad (12)$$

as for an even-numbered a.h. Of the n π -electrons, $n-1$ will be allotted in pairs to the orbitals ψ_1 to $\psi_{\frac{1}{2}(n-1)}$, and the remaining electron to the m.o. $\psi_{\frac{1}{2}(n+1)}$ of zero energy.

Just as for an even-numbered a.h., we can see from the secular equations (3) that

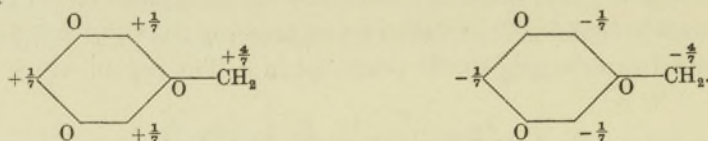
$$c_{r,n-j+1} = +c_{rj} \text{ or } -c_{rj} \quad (13)$$

according as atom r belongs to one set or the other. This means in particular that in the m.o. $\psi_{\frac{1}{2}(n+1)}$ the coefficients are zero for all the atoms of one set. The importance of this fact is conveniently illustrated by the benzyl radical; the coefficients $c_{r,\frac{1}{2}(n+1)}$ are



In the first place we may observe that the odd electron is distributed entirely over the atoms of one set, as suggested by the ordinary resonance theory. Secondly, the contribution of the odd electron to any bond is zero, this contribution being measured by $c_{r,\frac{1}{2}(n+1)} c_{s,\frac{1}{2}(n+1)}$. Thirdly, the removal of the odd electron or the insertion of another into the same m.o. will alter the electron densities at the atoms of one set, but not at those of the other. Now, as we shall show later, the electron density at every atom in an uncharged a.h. is unity; continuing with our example of benzyl

we conclude that the net charges $(1 - q_r)$ at the atoms of the cation and anion will be as follows:



Expressions for the mutual polarizabilities in terms of the coefficients and energies in the occupied m.o. can be derived by methods similar to those set out in Part I, and using equations (12) and (13). These expressions are

$$\pi_{r,s} = \pm 4 \sum_{j=1}^{\frac{1}{2}(n-1)} \sum_{k=1}^{\frac{1}{2}(n+1)} \frac{c_{rj} c_{sj} c_{rk} c_{sk}}{\epsilon_j + \epsilon_k}, \quad (14)$$

+ or - according as r and s are in the same set or not, and

$$\pi_{rs,tu} = 4 \sum_{j=1}^{\frac{1}{2}(n-1)} \sum_{\substack{k=1 \\ j < k}}^{\frac{1}{2}(n+1)} \frac{(c_{rj} c_{sk} - c_{sj} c_{rk})(c_{tj} c_{uk} - c_{uj} c_{tk})}{\epsilon_j + \epsilon_k}, \quad (15)$$

where r and t are taken to be in the same set.

SOME PROPERTIES OF THE MINORS OF THE SECULAR DETERMINANT

In the next section we shall draw conclusions about the electron densities, bond orders and mutual polarizabilities in an a.h. Before doing this, however, it is necessary to establish some results about the minors of the secular determinant for an a.h.

If atoms r and s are in the same set or are identical, we may suppose $r, s \leq h$, and write (see equation (4)):

$$\Delta_{r,s}(z) = \begin{vmatrix} -zI_{r,s} & A_{r,0} \\ \bar{A}_{0,s} & -zJ \end{vmatrix},$$

where letters before and after the comma in a suffix denote respectively rows and columns struck out: for instance $A_{r,0}$ denotes A with the r th row struck out but no column omitted. Multiplication of the first $h-1$ rows, and the last $n-h$ columns, by -1 gives the identity

$$\Delta_{r,s}(z) = (-)^{n-1} \Delta_{r,s}(-z). \quad (16)$$

Therefore if n is even, $\Delta_{r,s}(z)$ is a sum of odd powers of z , and if n is odd, of even powers of z .

On the other hand, if r and s belong to different sets, we may suppose that $r \leq h < s$, and write

$$\Delta_{r,s}(z) = \begin{vmatrix} -zI_{r,0} & A_{r,s} \\ \bar{A} & -zJ_{0,s} \end{vmatrix}.$$

Multiplication of the first $h-1$ rows and then the last $n-h-1$ columns by -1 shows that

$$\Delta_{r,s}(z) = (-)^n \Delta_{r,s}(-z). \quad (17)$$

Therefore in this case $\Delta_{r,s}(z)$ is a sum of even or odd powers of z according as n is even or odd.

We may summarize our knowledge of the oddness or evenness of $\Delta(z)$ and its minors in table 1.

TABLE 1

	n even	n odd	
$\Delta(z)$	even	odd	(5)
$\Delta_{r,s}(z)$ with r, s identical or in same set	odd	even	(16)
$\Delta_{r,s}(z)$ with r, s in different sets	even	odd	(17)

ELECTRON DENSITIES AND BOND ORDERS IN ALTERNANT HYDROCARBONS

We shall now prove some results about electron densities and bond orders in alternant hydrocarbons. By equation (43) of Part I

$$q_r = 1 - \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\Delta_{r,r}(iy)}{\Delta(iy)} dy, \quad (18)$$

the principal value being taken if we are considering an odd-numbered a.h. But from table 1 we see that $\Delta_{r,s}(z)/\Delta(z)$ is an odd function if atoms r and s are in the same set or are identical. Therefore the integral is zero and

$$q_r = 1. \quad (19)$$

Hence *the electron density is unity at every atom in an a.h.* That is, the net charge $(1 - q_r)$ is zero at every atom in an a.h. This was proved in a different way by Coulson

Rushbrooke, and is an important result for several reasons. First, it means that by assuming the coulomb integrals of all the carbon atoms equal we obtain a self-consistent field, so that the condition of minimal energy is satisfied within the limits of our variational treatment. Secondly, it shows that there is no piling up of charge on single atoms in an a.h., so that we should expect their dipole moments to be very small. Thirdly, it leads us to suppose that the differences in chemical reactivity between different positions are due to second-order effects, viz. differences in the self-polarizabilities of different positions. Fourthly, we can infer at once that mobile bond orders in an a.h. cannot exceed unity, since by equation (70) of Part I

$$p_{rs}^2 \leq q_r q_s = 1. \quad (20)$$

That is to say, no double bond in an alternant hydrocarbon can be more unsaturated than the double bond in ethylene, where $p = 1$.

ATOM-BOND POLARIZABILITIES

The polarizability of an atom r by a bond $s-t$, and of a bond $s-t$ by an atom r were defined in Part I by the equations

$$\pi_{r,st} = \frac{\partial q_r}{\partial \beta_{st}}, \quad \pi_{st,r} = \frac{\partial p_{st}}{\partial \alpha_r},$$

and it was proved that

$$\pi_{r,st} = 2\pi_{st,r}.$$

But in an alternant hydrocarbon, by equation (19), q_r is constant at unity, independently of the value of β_{st} ; therefore

$$\pi_{r,st} = 0 = \pi_{st,r}. \quad (21)$$

This result can also be seen from the oddness of the integrand in equation (59) of Part I, by table 1 of this paper. Physically speaking it means that the introduction of a methyl group, for instance, does not change bond orders appreciably in an a.h., and that small changes in resonance integrals, such as occur during vibrations, do not produce fluctuations in electron density.

MUTUAL ATOM POLARIZABILITIES

The mutual polarizability of two atoms r and s was defined in Part I by the equation

$$\pi_{r,s} = \frac{\partial q_r}{\partial \alpha_s},$$

and it was proved that (Part I, equation (57))

$$\pi_{r,s} = \pi_{s,r} = \frac{1}{\pi} \int_{-\infty}^{\infty} \left(\frac{\Delta_{r,s}(iy)}{\Delta(iy)} \right)^2 dy. \quad (22)$$

But in an a.h., by the results in table 1, $\Delta_{r,s}(iy)/\Delta(iy)$ is imaginary or real according as atoms r and s are in the same set or opposite sets. Therefore the integral in (22) is positive or negative according as r and s are in opposite sets or the same set. Hence *in an alternant hydrocarbon the mutual polarizability of two atoms is positive or negative according as the atoms are separated by an odd or an even number of bonds.*

This is a result of great importance because it provides a clear theoretical basis for the experimental law of alternating polarity which we referred to earlier. This may be seen as follows. In an a.h., as proved above, all the electron densities are unity. Therefore if we replace one carbon atom in an a.h. by a hetero-atom h with coulomb term $\alpha_h (= H_{hh} - H_{CC})$, the altered values of q_r throughout the molecule are given approximately by

$$q_r = 1 + \pi_{r,h} \alpha_h. \quad (23)$$

But the values of $\pi_{r,h}$ are alternately $+$ and $-$ as r varies along any chain of unsaturated bonds, as just proved; therefore q_r is alternately greater and less than 1 throughout the molecule. Using our correlation between electron density and chemical reactivity we obtain a direct derivation of the law of alternating polarity.

In the above discussion we have confined our attention to hetero-molecules having the same number of π -electrons as the parent a.h. This is true for pyridine, for instance, which has six π -electrons like benzene; but it does not hold for aniline, which has eight π -electrons, whereas the parent benzyl radical has only seven. We shall extend our treatment to molecules of the aniline type later in this paper.

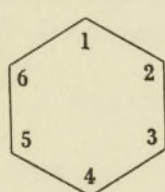
Again, we have supposed that hetero-substitution alters only one coulomb integral. In fact other parameters will be altered slightly, such as the coulomb terms of the atoms next to the hetero-atom, and the resonance integrals of the bonds at it. It would be more exact to write

$$q_r = 1 + \sum_s \pi_{r,s} \alpha_s + \sum_{tu} \pi_{r,tu} \delta \beta_{tu}. \quad (24)$$

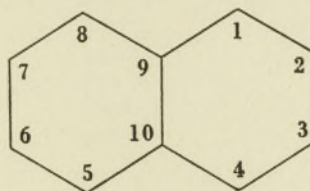
But as we have shown, all the terms $\pi_{r,tu}$ are zero; and the values of α_s will all be small except α_h . Therefore the relative values of q_r will still be governed mainly by $\pi_{r,h} \alpha_h$, and the other terms $\pi_{r,s} \alpha_s$ will not alter the general picture.

EXAMPLES: BENZENE AND NAPHTHALENE

In the present section we shall apply our general results to benzene and naphthalene, both of which are obviously alternant hydrocarbons. We shall follow the usual convention in numbering the atoms in these molecules, namely, as follows:



benzene



naphthalene

The coefficients in the m.o., taken in their real forms, are well known for benzene. They are, in our present notation,

$$\begin{aligned} c_{11} = c_{21} = c_{31} = c_{41} = c_{51} = c_{61} &= \sqrt{\frac{1}{6}}, & \epsilon_1 &= 2\beta; \\ c_{12} = 0 = c_{42}, & c_{22} = \frac{1}{2} = c_{32}, & c_{52} = -\frac{1}{2} = c_{62}, & \epsilon_2 = \beta; \\ c_{13} = \sqrt{\frac{1}{3}}, & c_{23} = \sqrt{\frac{1}{12}} = c_{63}, & c_{33} = -\sqrt{\frac{1}{12}} = c_{53}, & c_{43} = -\sqrt{\frac{1}{3}}, & \epsilon_3 &= \beta. \end{aligned}$$

For the unoccupied m.o. the energies are $-\beta$, $-\beta$, -2β , and the coefficients (see equation (8)) have opposite signs to those in the corresponding m.o., for every alternate atom. The electron densities are given by

$$q_r = 2 \sum_{j=1}^3 c_{rj}^2 = 1,$$

as they must be by equation (19).

The mutual atom polarizabilities are quickly calculated from (9); the mutual polarizability of *para* carbon atoms is $\pi_{1,4} = -11/108\beta$, of *meta* atoms $\pi_{1,3} = 1/108\beta$, and of *ortho* carbon atoms $\pi_{1,2} = -17/108\beta$; the self-polarizability $\pi_{1,1}$ of a carbon atom is $43/108\beta$. Particularly interesting is the low value of $\pi_{1,3}$, which means that the inductive effect hardly operates at all between *meta*-positions. The atom-bond polarizabilities are of course zero, by equation (21).

Hückel (1932) calculated the energies and coefficients of the molecular orbitals in naphthalene, assuming that the resonance integrals of all the bonds were equal to some value β . The electron densities calculated from these coefficients are unity, and the atom-bond polarizabilities zero, as they must be by equations (19) and (21). The mutual atom polarizabilities are most easily calculated from equation (9). They are given in table 2, where each number is to be multiplied by $1/\beta$. It is interesting to note that the interactions between atoms in different rings are much smaller than those between atoms in the same ring, as suggested by the chemical evidence.

TABLE 2. MUTUAL ATOM POLARIZABILITIES IN NAPHTHALENE
(THE FIGURE GIVEN IS $\pi_{r,s} \times \beta$)

	$s = 1$	2	9
$r = 1$	0.443	-0.213	-0.089
2	-0.213	0.405	0.007
3	0.018	-0.110	-0.049
4	-0.139	0.018	0.004
5	-0.023	0.007	0.004
6	0.007	-0.033	-0.049
7	-0.033	0.000	0.007
8	0.027	-0.033	-0.089
9	-0.089	0.007	0.330
10	0.004	-0.213	-0.077

These values illustrate well the law of alternating polarity, and may be used in estimating the charge distributions in hetero-derivatives of benzene and naphthalene. Let us take quinoline as an example, using the parameters quoted by Longuet-Higgins & Coulson (1947), in which the nitrogen atom is at position 1. To successive degrees of approximation we may calculate the electron densities as follows:

- (a) from the equation $q_r = 1 + \pi_{r,1} \alpha_1$, with $\alpha_1 = 2\beta$,
- (b) from the equation $q_r = 1 + \pi_{r,1} \alpha_1 + \pi_{r,2} \alpha_2 + \pi_{r,9} \alpha_9$, with $\alpha_1 = 2\beta$, $\alpha_2 = \beta/4 = \alpha_9$,
- (c) by direct solution of the secular equations (Part I, equation (10)) using the same values of $\alpha_1, \alpha_2, \alpha_9$.

The values of q_r obtained by these three methods are compared in table 3. The results of (a) and (b) agree with those of (c) in the following important respects:

- (i) Of the electron densities that at the nitrogen atom is by far the largest.
- (ii) The other electron densities lie close to unity except for q_2 and q_4 , which are considerably less than 1.
- (iii) The electron densities alternate in magnitude as we move along any bond path in the molecule.

Now the most important features of the chemistry of quinoline have already been correlated with the values of q_r calculated by method (c) (Longuet-Higgins & Coulson 1947); therefore the enhanced coulomb integral of atom 1 is undoubtedly the most important single factor governing the chemistry of this molecule.

TABLE 3. ELECTRON DENSITIES IN QUINOLINE

	method	(a)	(b)	(c)
$r = 1$		1.886	1.810	1.633
2		0.573	0.676	0.789
3		1.035	0.996	0.978
4		0.721	0.727	0.772
5		0.953	0.956	0.958
6		1.015	0.994	0.989
7		0.933	0.935	0.947
8		1.053	1.023	1.003
9		0.822	0.907	0.959
10		1.007	0.976	0.973

APPLICATION OF THE THEORY TO THE POLYENES

The polyenes (general formula C_nH_{n+2}) have been treated in some detail by Coulson (1939), who solved the secular equations in the general case. We shall use his results as a basis for calculating mutual polarizabilities in these molecules.

The secular equations are satisfied by n energy-values ϵ_j and sets of coefficients c_{rj} , given by

$$\epsilon_j = 2\beta \cos\left(\frac{j\pi}{n+1}\right), \quad c_{rj} = \sqrt{\left(\frac{2}{n+1}\right)} \sin\left(\frac{rj\pi}{n+1}\right), \quad (25)$$

Since a polyene is an alternant hydrocarbon, the electron density at every atom is 1, and the atom-bond polarizabilities are all zero. The mutual polarizability of a pair of atoms in a polyene is given by equation (57) of Part I, namely,

$$\pi_{r,s} = \frac{1}{\pi} \int_{-\infty}^{\infty} \left(\frac{\Delta_{r,s}(iy)}{\Delta(iy)} \right)^2 dy. \quad (22)$$

Let us denote the secular determinant for the polyene $CH_2(CH)_{n-2}CH_2$ by D_n (the suffix here must not be confused with the pair of suffixes denoting omission of rows and columns); that is, we put

$$\begin{vmatrix} -\epsilon & \beta & 0 & 0 & 0 \\ \beta & -\epsilon & \beta & 0 & 0 \\ 0 & \beta & -\epsilon & \beta & 0 \\ 0 & 0 & \beta & -\epsilon & \beta \\ 0 & 0 & 0 & \beta & -\epsilon \end{vmatrix} \quad (n \text{ rows and columns}) = D_n(\epsilon).$$

Then by Laplace's expansion of a determinant, $(D_n)_{r,s}$ is equal to $\beta^{s-r} D_{r-1} D_{n-s}$.

Therefore
$$\pi_{r,s} = \frac{\beta^{2s-2r}}{\pi} \int_{-\infty}^{\infty} \left(\frac{D_{r-1}(iy) D_{n-s}(iy)}{D_n(iy)} \right)^2 dy.$$

Replacing y by $2i\beta \cos \theta$, and using the identity

$$D_n(-2\beta \cos \theta) = \beta^n \sin(n+1)\theta / \sin \theta,$$

we obtain

$$\pi_{r,s} = \frac{1}{\beta\pi} \int_{-\infty}^{\infty} \frac{\sin^2 a\theta \sin^2 b\theta}{\sin^2 c\theta \sin^2 \theta} d(2i \cos \theta),$$

where $a = r$, $b = n - s + 1$ and $c = n + 1$. This may be written

$$\pi_{r,s} = -\frac{1}{\beta\pi} \int_{-\infty}^{\infty} \frac{(z^a - z^{-a})^2 (z^b - z^{-b})^2}{(z^c - z^{-c})^2 (z - z^{-1})^2} d\{i(z + z^{-1})\},$$

where $z = e^{i\theta}$. Now as z goes from ∞i to $0i$ along the imaginary axis, $i(z + 1/z)$ goes steadily from $-\infty$ to $+\infty$. Therefore

$$\pi_{r,s} = -\frac{i}{\beta\pi} \int_{\infty i}^0 \frac{(z^a - z^{-a})^2 (z^b - z^{-b})^2 (1 - z^{-2})}{(z^c - z^{-c})^2 (z - z^{-1})^2} dz.$$

But the integral is unaltered if we write $1/z$ for z as variable of integration; therefore

$$\int_{-\infty i}^{-i} = \int_{-i}^0 = \int_0^i = \int_i^{\infty i}.$$

It follows that

$$\pi_{r,s} = \frac{2i}{\beta\pi} \int_0^i \frac{z^{2(c-a-b)} (z^{2a} - 1)^2 (z^{2b} - 1)^2}{(z^{2c} - 1)^2 (z^2 - 1)} dz. \quad (26)$$

We can simplify the above expression under certain limiting conditions, using the fact that if $|z| < 1$, z^N tends to zero as N tends to infinity.

(a) If we have a pair of atoms far from the ends of a long polyene chain, n , r and s will all be large, but not necessarily $s - r$. Therefore

$$\pi_{r,s} \simeq \frac{2i}{\beta\pi} \int_0^i \frac{z^{2(s-r)} dz}{z^2 - 1} = \frac{(-)^{s-r} 2}{\beta\pi} \int_0^1 \frac{x^{2s-2r}}{1 + x^2} dx. \quad (27)$$

This takes the values

$$\frac{1}{2\beta}, \quad \frac{2}{\beta\pi} \left(\frac{\pi}{4} - 1 \right), \quad \frac{2}{\beta\pi} \left(\frac{\pi}{4} - 1 + \frac{1}{3} \right), \quad \frac{2}{\beta\pi} \left(\frac{\pi}{4} - 1 + \frac{1}{3} - \frac{1}{5} \right), \quad \dots$$

$$= 0.500, \quad -0.137, \quad 0.076, \quad -0.052, \quad 0.039, \quad -0.032 \times 1/\beta,$$

when $s - r = 0, 1, 2, 3, \dots$

(b) When one atom (r) is the first in a long polyene chain and the other (s) is not far from it, the expression for $\pi_{r,s}$ is approximately

$$\frac{2i}{\beta\pi} \int_0^i \frac{z^{2(s-1)} (z^2 - 1) dz}{(z^{2c} - 1)^2 (z^2 - 1)} = \frac{(-)^{s-1} 8s}{\beta\pi (4s^2 - 1)}. \quad (28)$$

This takes the values $0.85, -0.34, 0.22, -0.15, 0.10 \times 1/\beta$ when $s - r = 0, 1, 2, \dots$

(c) We can obtain an explicit expression for $\pi_{r,s}$ in a finite polyene chain when $r = 1$, as follows:

An alternative expression for $\pi_{r,s}$ is (see equation (26))

$$\frac{1}{2\pi i \beta} \int_{\infty i}^{-\infty i} \frac{z^{2(c-a-b)} (z^{2a} - 1)^2 (z^{2b} - 1)^2}{(z^{2c} - 1)^2 (z^2 - 1)} dz.$$

If this is regarded as part of a contour integral, the other part being a zero integral over the infinite semicircle, we see that it is equal to $1/\beta$ times the sum of the residues of the integrand at its poles to the right of the imaginary axis. (We shall assume n to be even so that c is odd and there are no poles on the imaginary axis.) These poles occur at

$$z_m = \exp(mi\pi/c), \quad \text{where } m = \pm 1, \pm 2, \dots, \pm(c-1)/2,$$

but there is no pole at $z = 1$, since there the numerator vanishes more strongly than the denominator. The residue at z_m is

$$\frac{(z_m^a - z_m^{-a})^2 (z_m^b - z_m^{-b})^2}{4c^2(z_m - z_m^{-1})} \left\{ 2a \left(\frac{z_m^a + z_m^{-a}}{z_m^a - z_m^{-a}} \right) + 2b \left(\frac{z_m^b + z_m^{-b}}{z_m^b - z_m^{-b}} \right) - \left(\frac{z_m + z_m^{-1}}{z_m - z_m^{-1}} \right) \right\}.$$

Therefore

$$\pi_{r,s} = \frac{-4^{\frac{1}{2}(c-1)}}{\beta c^2} \sum_{m=1}^{\frac{c-1}{2}} \frac{\sin^2 \frac{m\pi}{c} \sin^2 \frac{mb\pi}{c}}{\sin \frac{m\pi}{c}} \left\{ 2a \cot \frac{m\pi}{c} + 2b \cot \frac{mb\pi}{c} - \cot \frac{m\pi}{c} \right\}. \quad (29)$$

Remembering that $a = r$, $b = n - s + 1$, $c = n + 1$, we can simplify equation (29) when $r = 1$, obtaining for $\pi_{1,s}$ the expression

$$\frac{(-)^{s-1}}{2\beta(n+1)^2} \left\{ (2n-2s+1) \operatorname{cosec} \frac{(2s+1)\pi}{2n+2} + (2n-2s+3) \operatorname{cosec} \frac{(2s-1)\pi}{2n+2} + (-)^s 2 \operatorname{cosec} \frac{\pi}{2n+2} \right\}. \quad (30)$$

In all these special cases we see that the mutual polarizability of a pair of atoms in a polyene decreases with their distance apart, as well as alternating in sign as required by the law of alternating polarity. The same is true for pairs of bonds, as we shall show in a later paper.

We shall close this section on the polyenes with a table of mutual atom polarizabilities in butadiene and hexatriene (see table 4). It will be observed that in both these molecules the terminal atoms have the highest self-polarizabilities, so that we should expect them to be the initial points of attack in chemical reactions, at least of the heterolytic type.

TABLE 4. MUTUAL POLARIZABILITIES OF ATOMS IN BUTADIENE AND HEXATRIENE
(THE FIGURES GIVEN ARE TO BE MULTIPLIED BY $1/\beta$)

	$s =$	1	2	3	4		
$r = 1$		0.626	-0.402	0.045	-0.268		
2		-0.402	0.402	-0.045	0.045		
			butadiene				
	$s =$	1	2	3	4	5	6
$r = 1$		0.685	-0.376	0.083	-0.221	0.015	-0.187
2		-0.376	0.389	-0.034	0.007	-0.002	0.015
3		0.083	-0.034	0.470	-0.304	0.007	-0.221
			hexatriene				

OTHER TYPES OF HETERO-MOLECULE

So far we have discussed only hetero-molecules such as pyridine and quinoline which have the same number of electrons as the corresponding alternant hydrocarbon. We shall now consider hetero-molecules such as aniline and chlorobenzene, derived from an odd-numbered alternant hydrocarbon by replacement of one carbon by a hetero-atom, the total number of π -electrons being increased by one. The secular equations for such a hetero-molecule differ from those of the corresponding a.h. in having a negative value of α for one atomic orbital.

Before applying our general formulae we must make sure that the occupied m.o. all have negative energies. Now by Part I, equation (22),

$$\frac{\partial \epsilon_j}{\partial \alpha_r} = c_{rj}^2 \geq 0. \quad (31)$$

Therefore, since the coulomb term α_h for the hetero-atom is negative, the energy of a m.o. in the hetero-molecule is negative if the corresponding m.o. in the parent hydrocarbon has negative energy. Now the only m.o. of the parent hydrocarbon with non-negative energy is $\psi_{\frac{1}{2}(n+1)}$, which has zero energy. So if the hetero-atom replaces a carbon atom r for which $c_{r, \frac{1}{2}(n+1)} = 0$, $\epsilon_{\frac{1}{2}(n+1)}$ will be zero in the hetero-molecule also, since the value of α_r will not affect that m.o. However, it seems that for all real hetero-molecules this situation does not arise, so that $\epsilon_j < 0$ for all the m.o. Further, in the hetero-molecules we are considering all the electrons are paired; hence our general equations may be applied.

Now by equation (43) of Part I

$$q_s = 1 - \frac{1}{\pi} \int \frac{\Delta_{s,s}^*}{\Delta^*} dy, \quad (32)$$

where Δ^* refers to the hetero-molecule, the limits of integration are $-\infty$ to $+\infty$, and the determinants in an integral are understood to be functions of iy . If Δ refers to the parent a.h., we may expand this and write

$$\begin{aligned} q_s &= 1 - \frac{1}{\pi} \int \frac{\Delta_{s,s} + \alpha_h \Delta_{hs,hs}}{\Delta + \alpha_h \Delta_{h,h}} dy \\ &= 1 - \frac{1}{\pi} \int \alpha_h \frac{\Delta_{hs,hs} \Delta - \Delta_{s,s} \Delta_{h,h}}{\Delta^2 - \alpha_h^2 \Delta_{h,h}^2} dy - \frac{1}{\pi} \int \frac{\Delta_{s,s} \Delta - \alpha_h^2 \Delta_{hs,hs} \Delta_{h,h}}{\Delta^2 - \alpha_h^2 \Delta_{h,h}^2} dy. \end{aligned}$$

Now Δ^2 and $\Delta_{h,h}^2$ are even functions of y , and $\Delta_{s,s}$ and $\Delta_{hs,hs} \Delta_{h,h}$ are odd functions of y ; therefore the second integral is zero. But by Jacobi's theorem

$$\Delta_{hs,hs} \Delta - \Delta_{s,s} \Delta_{h,h} = -\Delta_{h,s}^2.$$

Therefore

$$q_s = 1 + \frac{\alpha_h}{\pi} \int \frac{\Delta_{h,s}^2}{\Delta^2 - \alpha_h^2 \Delta_{h,h}^2} dy. \quad (33)$$

Now by table 1 the last integral is negative or positive according as h and s are in the same set or not. Therefore when $\alpha_h < 0$, q_s is greater or less than 1 according as h and s are in the same set or not. This shows that our interpretation of the experimental law of alternating polarity does not depend on α_h being small, and that it applies when the number of π -electrons is one greater than the number of atomic orbitals involved in the conjugation.

Equation (33) holds for all values of α_h . However, if we may neglect α_h^2 in the denominator, we obtain

$$q_s \simeq 1 + \frac{\alpha_h}{\pi} \int \frac{\Delta_{h,s}^2}{\Delta^2} dy = 1 + \pi_{s,h} \alpha_h.$$

As we should expect, this is simply equation (23). But since $\Delta^2(iy)$ and $\Delta_{h,h}^2(iy)$ have opposite signs, it also follows that use of the simple formula (23) instead of the more accurate (33) always exaggerates the magnitudes, but does not change the signs, of the charge displacements $q_s - 1$.

It is worth noting that in molecules such as aniline, where n is odd

$$\sum_{s=1}^n q_s = n + 1, \quad (34)$$

so that q_s may be considerably greater than one for the hetero-atom and the other atoms in the same set. An electron density of 2 on the hetero-atom would correspond to the classical valence diagram, which takes no account of the participation of the 'unshared pair' in the aromatic system. When n is even, on the other hand,

$$\sum_{s=1}^n q_s = n, \quad (35)$$

that is to say, the available electrons are less lavishly distributed, so that the excess electron density on the hetero-atom must be compensated by a considerable positive charge on one or more atoms of the other set; this explains why molecules such as pyridine are most susceptible to anionoid reagents, and those such as aniline to cationoid reagents.

CONCLUSION

Although the law of alternating polarity as we have derived it holds strictly only for a molecule whose secular determinant differs from that of an alternating hydrocarbon by one coulomb term, it will be expected to apply locally in more complex molecules in view of the rapid falling off of mutual polarizabilities with distance. In molecules where there are two or more hetero-atoms we may still use mutual atom polarizabilities for calculating electron densities, taking the corresponding hydrocarbon as basis for a first-order perturbation treatment. This may save a great deal of labour in enabling us to predict roughly electron densities in a number of different hetero-molecules derived from the same hydrocarbon.

The theory of chemical orientation put forward in this paper does not conflict in any way with the current qualitative resonance picture; but it makes possible the assessment of the relative extents to which substitution will affect different positions in a molecule, a problem which has hitherto eluded satisfactory treatment by the resonance theory.

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A study by a double-refraction method of the development of turbulence in a long circular tube

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A streaming double-refraction method was employed to examine the flow in a long glass tube of a very weak solution of benzopurpurin in water. Two kinds of turbulent entry were used: with one, laminar flow at a Reynolds number of about 1900 was observed at cross-sections more than 120 diameters from the entry; with the other the corresponding distance was 90 diameters. The nature of the breakdown of laminar flow at a cross-section was found to depend upon the kind of entry and upon the distance of the cross-section from the inlet. The development of complete turbulence at various cross-sections was also investigated.

1. INTRODUCTION

In a previous paper (Binnie 1945) an account was given of an investigation of the onset of turbulence in a liquid flowing through a straight circular glass tube. Use was made of the fact that certain liquids exhibit the property of streaming double-refraction. A beam of polarized light was arranged to traverse a diameter of the tube, the nicols being set to give extinction when the liquid was stationary. With the liquid in motion at a low velocity it was found that a steady beam of light emerged, the intensity of which depended upon the velocity of the liquid. When, however, the velocity exceeded a certain limit the beam became unsteady, and the disturbances are believed to indicate the development of turbulence.

The motion of a liquid has often been examined by introducing into it some form of indicator such as a thread of potassium permanganate (Reynolds 1883), oil drops