92. *Conjugation of a Hetero-atom across a Single Bond.*

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The molecular-orbital method is used to provide a general discussion of the way in which the conjugation of a hetero-atom (*e.g.*, a halogen) with a conjugated or aromatic hydrocarbon residue (*e.g.*, phenyl) depends on the electronegativity of the hetero-atom and the resonance integral between the hetero-atom and the carbon atom to which it is attached. This conjugation is shown to depend more strongly on the resonance integral than has often been supposed. The dependence is different according as we measure the extent of the conjugation in terms of delocalisation energy, bond order, or charge migration.

When two conjugated systems AH and BH are joined together, as in Fig. 1, by elimination of the hydrogen atoms at *a* and *b*, we speak of an extended conjugation across the " single " bond *a*–*b*. In this process A and B may be hydrocarbon residues, such as phenyl groups giving diphenyl; or one of them may be a single atom with π-electrons available to extend the conjugation path previously limited to the other residue. An example of this type is a monosubstituted benzene, such as when A is phenyl and B is chlorine, giving chlorobenzene. In this latter case the chlorine atom contributes two electrons to the total conjugating system. If we adopt the molecular-orbital description of this phenomenon, we speak of a greater degree of delocalisation of the π-electrons; in the alternative valence-bond description we speak of the introduction of new " structures," in which the bond *a*–*b* appears double, and there may or may not be charges on some of the atoms of A and B. Conjugation of this kind should be reflected in (1) the bond order of the bond *a*–*b*, (2) the resonance energy, or (better) delocalisation energy, which results, and (3) the charge displacements associated with the final molecule, when compared with the composite parts, AH and BH.

Fig. 1.

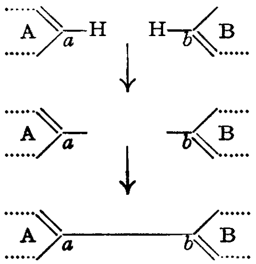
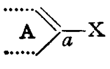


Fig. 2.



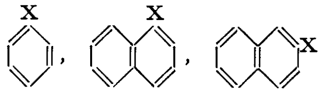
The situation in which A and B are alternant hydrocarbons has already been fairly fully discussed. Thus a large number of particular examples have been studied numerically by Coulson and Jacobs (*J.*, 1949, 1983) who showed that the larger the two residues, the greater was the bond order of *a–b*. It has also been discussed theoretically by Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1948, *A*, **195**, 188), who showed that if β_{ab} and p_{ab} are the resonance integral and π-bond order in the final bond *a–b*, and if R_{ab} is the conjugation energy across *a–b* (*i.e.* the extra delocalisation energy on forming A–B) then, in a close approximation :

$$R_{ab} \propto p_{ab} \cdot \beta_{ab} \propto \beta_{ab}^2 \times \sqrt{\pi_{a,a}} \times \sqrt{\pi_{b,b}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this formula $\pi_{a,a}$ and $\pi_{b,b}$ are the self-polarisabilities of the centres *a* and *b* in the residues A and B, respectively (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39). It was as a result of (1) that these authors identified $\pi_{a,a}$ and $\pi_{b,b}$ as the conjugating powers of A and B, though it now seems as if $\sqrt{\pi_{a,a}}$ would have been a better definition. In all this work the overlap integral between adjacent π atomic orbitals was tacitly neglected; but de Heer (*Phil. Mag.*, 1950, **41**, 370) showed that the result (1) was still substantially valid even when it was included, provided that the revised definitions of bond order, charge, and polarisability due to Chirgwin and Coulson (*Proc. Roy. Soc.*, 1950, *A*, **201**, 196) were used.

In all these discussions the two fragments A and B have been alternant hydrocarbons, so that there is no net flow of charge from A to B, or *vice versa*. One of our objects in this paper is to investigate this charge migration, and, in particular, to discover what factors (*e.g.* coulomb terms, resonance integrals, polarisabilities) are most effective in determining its magnitude. For this purpose we shall consider the case (Fig. 2) where A is an alternant hydrocarbon and B is a single hetero-atom, frequently a halogen. When B is a single atom it will be convenient to use a different symbol, and refer to it as X. We choose this type of molecule because it is amenable to theoretical treatment, and it is at the same time a prototype for all conjugation across a single bond involving at least one hetero-molecule. The applications of this study are quite numerous. Thus, on the one hand, by keeping X unchanged but by varying A, we discuss charge, bond order, and energy in a series such as type i, and, on the other hand, by keeping A unchanged, but by varying X, we are able to make a comparative study of a series of compounds, such as the phenyl halides (type ii).

$CH_2{=}CHX$,



. . . . . (type i)

C_6H_5F, C_6H_5Cl, C_6H_5Br, C_6H_5I . . . . . . (type ii)

A practical example of the type (i) series occurs when X is a bromine atom. Pullman, Rumpf, and Kieffer (*J. Chim. phys.*, 1948, **45**, 150) have indicated that the charge density on the bromine atom is a predominant factor in determining the rate of isotopic bromine-exchange reactions. A second example is provided by α- and β-chloronaphthalene, where Ketelaar and van Oosterhout's detailed numerical calculations (*Rev. Trav. chim.*, 1946, **65**, 449) show a larger resonance energy in the former than in the latter. This conclusion could have been immediately predicted on the basis of equation (2) below. Another example is when X is OH, for the charge shift should measure to some extent the acidity of the corresponding phenols. Similarly, when X is NH_2 we expect to be able to discuss such quantities as the difference in basicity of α- and β-naphthylamine. [However, some caution is needed in this latter case because dipole-moment evidence suggests strongly that the three bonds at the nitrogen atom are not coplanar, so that the two conjugating electrons from the nitrogen are not strictly π-electrons, but have approximately tetrahedral hybrid forms which do bear a slight resemblance to π-orbitals. Our later general analysis will probably still apply, though perhaps with a reduced resonance integral β_{ax}. A somewhat similar caution is needed when X is a sulphide radical, such as SH, for as Longuet-Higgins (*Trans. Faraday Soc.*, 1949, **45**, 173) and Moffitt (*Proc. Roy. Soc.*, 1950, *A*, **200**, 409) have shown, *d*-electrons may play an important rôle in the type of bond formed.] As regards molecules of type (ii) a satisfactory analysis of the charge shifts is much to be desired, both qualitatively and quantitatively. For example, in qualitative discussions by organic chemists, such as in the consideration of mesomeric dipole moments, one often finds such statements as : " since fluorine is more electronegative than chlorine, chlorine more electronegative than bromine, and bromine than iodine, the tendency of these atoms to send their two π-electrons into the benzene ring increases from fluorine to iodine." And in quantitative spectral studies variations in the parameter α which (see later) measures the electronegativity of X are often taken to be a sufficiently comprehensive factor as to be able to describe the frequency shifts that occur on substitution. It is true that Matsen (*J. Amer. Chem. Soc.*, 1950, **72**, 5243), when attempting such a discussion, found that in certain instances (including the halogenobenzenes) he was unable to absorb all differences in resonance integrals and all inductive effects in this one term; and he was obliged to introduce a second parameter, k' in our equation (2), to allow for this. The present analysis shows why this is necessary and in particular it underlines the significance of variations in the resonance integral, β_{ax}, which may be even more important than variations in α. This point does not appear to have been sufficiently stressed hitherto, although it could have been concluded from a number of numerical calculations made at various times by various authors.

Some analysis of the general problem of molecules AX has already been given by the present writers (*Trans. Faraday Soc.*, 1951, **47**, 681), who obtained a formula [formula (2), below] for the delocalisation energy due to the extra conjugation. This formula was closely similar to, though not identical with, the hydrocarbon formula (1).

$$-R_{ab} = k' + 0{\cdot}67(\pi_{a,a}/\alpha)^{\frac{1}{2}}\beta_{ab}{}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

[$\pi_{a,a}$ and β_{ab} have the same meaning as in (1). α is the coulomb term of the hetero-atom X, and k' is a constant measuring the inductive effect of X on the coulomb term of carbon atom a.]

We shall return to this formula later. From our present point of view it suffers from the drawback that it is not valid for small values of α, and it is obtained by a type of analysis which is not easily extended to deal with the bond order, p_{ax}, and charge distribution, q_x. We shall therefore develop alternative formulæ of a similar kind, applicable to all three measures of the conjugation. Afterwards we shall discuss their significance.

Let us return to Fig. 2, in which X is a group such as a halogen, and A is an alternant hydrocarbon. Then, in the notation used by Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1947, *A*, **191**, 39), let $\Delta(\varepsilon)$ be the secular determinant of the combined system, and $A(\varepsilon)$ that of the hydrocarbon residue A. Further, let α denote the coulomb term of the atom X, all energies being measured relative to a π-electron of a carbon atom. For the moment we shall not introduce any inductive effect, so that the coulomb term of atom a is supposed to be the same in the system AX as it was originally in the unsubstituted hydrocarbon AH. Later on, however, we shall use the symbol k' [Coulson and de Heer, equation (3)] to denote the change in coulomb term at atom a when the presence of X induces an increase in effective electronegativity of this atom. We may expect k' to be much smaller numerically than α, and to range from molecule to molecule in a closely similar way. The notation $\Delta_{r,s}$ or $A_{r,s}$ will mean that in each case the r'th row and s'th column have been struck out of the determinants. We have introduced these definitions because they allow us to use certain formulæ for q_x, the total mobile charge on X; for R_{ax}, the conjugation energy; and for p_{ax}, the mobile bond order of the bond a–X, which were given by Coulson and Longuet-Higgins (*loc. cit.*). The first of these formulæ is :

$$q_x = 1 - \frac{1}{\pi i}\int_{-\infty i}^{\infty i} \frac{\Delta_{x,x}}{\Delta} \, . \, dz \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

However, $\Delta_{x,x}$ is simply A, and, with the usual neglect of all overlap integrals, we may write $\Delta(z) = (\alpha - z) \, . \, A(z) - \beta_{ax}{}^2 \, . \, A_{a,a}(z)$, so that

$$q_x = 1 - \frac{1}{\pi i}\int \frac{A(z)}{(\alpha - z) \, . \, A(z) - \beta_{ax}{}^2 \, . \, A_{a,a}(z)} \, . \, dz \quad . \quad . \quad . \quad (4)$$

No further general progress is possible with this integral, but if we may expand the integrand in powers of β_{ax} (effectively β_{ax}/β, where β is the normal carbon–carbon resonance integral), we have an approximation which has frequently been used, and (see later) shown to be remarkably good. Accepting this simplification, which should certainly serve to indicate the relative importance of quantities such as α and β_{ax}, we find that

$$q_x = 1 - \frac{1}{\pi i}\int_{-\infty i}^{\infty i}\left[\frac{1}{\alpha - z} + \frac{\beta_{ax}{}^2 \, . \, A_{a,a}(z)}{(\alpha - z)^2 \, . \, A(z)} + \ldots .\right]\mathrm{d}z$$

The first integral gives $-\pi i$, and the second can be simplified since $A(z)$ and $A_{a,a}(z)$ are polynomials of even and odd degree, respectively, in z. We have, finally,

$$q_x = 2 + \frac{2\alpha\beta_{ax}{}^2}{\pi}\int_{\infty}^{\infty}\frac{-iy \, . \, A_{a,a}\,(iy)}{(\alpha^2 + y^2)^2 \, . \, A(iy)} \, . \, \mathrm{d}y + \ldots . \quad . \quad . \quad . \quad (5)$$

Since α is negative [otherwise the basic integral (3) is not valid] this means that a charge equal approximately to

$$\frac{-2\alpha\beta_{ax}{}^2}{\pi}\int_{-\infty}^{\infty}\frac{-\,iy \, . \, A_{a,a}(iy)}{(\alpha^2 + y^2)^2 \, . \, A(iy)} \, . \, \mathrm{d}y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

has migrated from X into the aromatic residue A.

If we now make the same calculation again, though including the inductive term k', we find, to the first degree in k', that the result in equation (6) still holds good. The earlier work by Coulson and de Heer, as expressed in equation (2), suggests that in this type of approximation we may regard the first-order term in k' as being on the same footing as the term in $\beta_{ax}{}^2$. This means that for our present purposes, we may retain equation (6) in its original form, whether or not the inductive effect is included.

A similar analysis may be applied to the asymptotic expansion of the conjugation energy, R. Equation (9) of Coulson and de Heer's paper shows us that this may be put in the form :

$$-R = k' + \frac{\beta_{ax}{}^2}{\pi}\int_{-\infty}^{\infty}\frac{A_{a,a}(iy)}{(\alpha - iy) \, . \, A(iy)} \, . \, \mathrm{d}y$$

This transforms to :

$$-\,R = k' + \frac{\beta_{ax}{}^2}{\pi}\int_{-\infty}^{\infty}\frac{iy \, . \, A_{a,a}(iy)}{(\alpha^2 + y^2) \, . \, A(iy)} \, . \, \mathrm{d}y \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In an exactly analogous way, we can adapt Coulson and Longuet-Higgins's equation (11) (*loc. cit.*, 1948) to give equation (8), which is valid whether or not the inductive effect is included. The result is :

$$p_{ax} = -\,\frac{\beta_{ax}}{\pi}\int_{-\infty}^{\infty}\frac{-\,iy \, . \, A_{a,a}(iy)}{(\alpha^2 + y^2) \, . \, A(iy)} \, . \, \mathrm{d}y + \ldots . \quad . \quad . \quad . \quad . \quad (8)$$

in which the next two terms on the right-hand side are multiples of $\beta_{ax}{}^3$ and $k'\beta_{ax}$.

Equations (6), (7), and (8) give us a measure of the conjugation, as reflected in charge flow, energy, and bond order, respectively. All three results are obtained by considering only the initial terms of a power-series expansion. However the second equation (for the energy) has been carefully discussed by Coulson and de Heer in an equivalent form to that which we have used, and they showed that for all reasonable values of the parameters it was valid to within a few per cent. We may therefore presume that the same is true for the other equations, (6) and (8). We shall therefore discuss all three equations together in terms of the variations which they predict with k', β_{ax}, and α.

In the first place we notice that the inductive effect, as measured by k', is only significant for the conjugation energy. It appears to exert only a second- or third-order effect on charge migration and bond order.

Next let us consider the limiting forms taken by equations (6)—(8) when the attached atom X is strongly electronegative, so that $|\alpha|$ is large. We see that :

the conjugation energy varies as β_{ax}^2/α^2 (excluding the term k'), the charge migration varies as β_{ax}^2/α^3, and the bond order varies as

$$\beta_{ax}/\alpha^2 \qquad \text{. . . . .} \qquad (9)$$

These three results show that in every case the conjugation across the bond depends on the resonance integral, β_{ax}, as much as on the coulomb term (or electronegativity), α. This means that any discussions which deal only with the coulomb term must necessarily be inadequate. The physical explanation of this is that whereas α measures the attraction for electrons of the atom X, β_{ax} measures the attraction of the bond *a*–X. In order that there may be effective conjugation, it is certainly necessary that β_{ax} should not be too small.

If we pass to the other extreme and consider the case where $|\alpha|$ is small, so that X is not very electronegative compared with carbon, instead of equation (9) we have that: the conjugation energy varies as β_{ax}^2 (excluding the term k'), the charge migration varies as $\beta_{ax}^2/(\beta_{ax}^2 + \text{constant})$, and the bond order varies as

$$\beta_{ax} \qquad \text{. . . . .} \qquad (10)$$

The only difficult formula here is that for the charge migration. It is not possible to let $\alpha \longrightarrow 0$ in equation (5) on account of convergence difficulties. Consequently we must return to equation (4), from which it may be shown that:

$$q_x = 1 + \frac{A(0)}{A(0) + \beta_{ax}^2 \,.\, A_{a,a}'(0)} \qquad \text{. . . . . . .} \qquad (11)$$

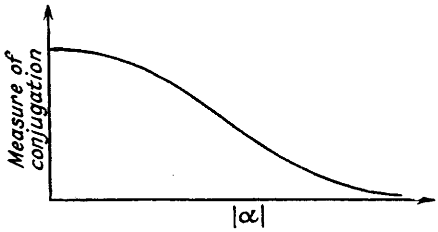
when α is identically zero. This implies that the charge migration $(2 - q_x)$ away from the atom X is:

$$\beta_{ax}^2 \,.\, A_{a,a}'(0)/[A(0) + \beta_{ax}^2 \,.\, A_{a,a}'(0)] \qquad \text{. . . . .} \qquad (12)$$

This is the result quoted in equation (10). In any actual example the numerical value of expression (12) may often be found most easily by a simple extension of the type of argument introduced by Longuet-Higgins (*J. Chem. Phys.*, 1950, **18**, 275).

For values of α intermediate between the two extreme values in (9) and (10) it is not hard to trace the variation of R (excluding k'), q_x, and p_{ax}. All three quantities are described by curves similar in general shape to that shown in Fig. 3. The details of these curves must obviously depend on the resonance integral, β_{ax}, and the choice of hydrocarbon, AH. In every case, however, β_{ax} plays at least as important a rôle as α, and often it is more important.

FIG. 3.



The results expressed by (9) and (10) show us clearly how it comes about that one single parameter such as α (Matsen's δ, *loc. cit.*) is unable to account for all those conjugation phenomena. For example it is quite evident from the form of the equations that variations in α cannot possibly absorb variations in β, though this may be approximately possible if we restrict our attention to just one of the three measures of conjugation. Any agreements with observation which are obtained in such a one-parameter way must be regarded as largely empirical.

The expressions (9) and (10) can also be used to throw light on certain resonance dipole moments. In a compound such as PhX it is reasonable to suppose that the difference $\alpha_x - \alpha_c$ (our previous α) is roughly proportional to the difference in electronegativities $|x_x - x_c|$, or at very least varies in the same general manner. Now Wheland ("Theory of Resonance," John Wiley, 1944, p. 132) has collected a table of experimental dipole moments. In particular he has compared the differences, $\mu_{\text{RX}} - \mu_{\text{PhX}}$, where X is a halogen and R is an alkyl group of approximately the same size as Ph (this is to give as nearly equal polarisabilities as possible in R and Ph, and to make the back-polarisations due to the residual charges on the halogens as nearly the same as we can, in the two molecules). It appears from Wheland's table that the difference, $\mu_{RX} - \mu_{PhX}$, has a value 0·58 D when X is iodine, an atom for which Pauling gives a zero electronegativity difference. Thus the resonance moment here cannot arise from the coulomb term, α_I. According to our present description the charge migration must be due to the smaller $|\beta|$ for the π electrons in C–I rather than for those in C=C. The direction, of course, is just what would have been expected on our theory. In this way we confirm the importance of β in the determinations of resonance effects across a " single " bond.

In addition to this we may compare resonance moments for the cases where X is either Cl, Br, or I; Wheland gives the corresponding numerical values as 0·42, 0·49, and 0·58 D. Now the positive ends of these dipoles are assuredly on, or very near to, the halogen, and the negative ends must be somewhere just inside the benzene ring. If we recognise that the C–X distances are 1·77, 1·91, and 2·10 Å, respectively, we see that the actual charge migrations responsible for these resonance moments must be very nearly equal in all three molecules. This equality of charge $(2 - q_x)$ must be compared with the corresponding electronegativity differences, which are far from being equal, and are actually 0·5, 0·3, and 0. It is true that the resonance moments which we have quoted must not be treated too seriously. For the choice of alkyl radical R is not unique, and, as Mulliken and Coulson have shown, the resolution of the total molecular dipole moment into σ- and π-contributions is complicated by homopolar dipoles and hybridisation dipoles. Nor is it completely accurate to infer the charge migrations simply by dividing the resonance moments by some effective separation of the positive and negative charges. But when all this is taken into account, it is still fair to conclude that the resonance moments are evidently not governed solely, or even chiefly, by electronegativity differences. When we recall that the bond energies of C–Cl, C–Br, and C–I, as given by Pauling, are respectively 67, 54, and 46 kcal./mole, so that the β_{0x} values will presumably follow a similar type of relationship, it is clear that there is strong experimental support for a charge-migration formula such as is implied in the expressions (9) and (10). A more precise numerical verification will only be possible when more is known than at present about the α's and β's between carbon and various hetero-atoms.

Reference must be made to the neglect of all overlap integrals. Now the works of Chirgwin and Coulson, of de Heer, and of Löwdin (*J. Chem. Phys.*, 1950, **18**, 365) all show that for alternant hydrocarbons the inclusion of these integrals makes absolutely no difference, and for certain mono-substituted ones, the difference is small, at least when equation (1) is applied. It seems fairly certain that this will also be true for the results of expressions (9) and (10). The most intuitive reason for this belief is that our formulæ relate essentially to the " initial stage " of a conjugation process. In such a stage the original alternant hydrocarbon is only slightly distorted, and we should therefore expect that conclusions which were valid for the alternant hydrocarbon itself would not thereby be gravely invalidated. This conclusion finds support from an " initial stage " calculation employing the technique suggested by Löwdin. We shall not reproduce the analysis, as it is of no great interest. But it can be shown, for example, that the charge migration is still given by an expression formally almost equivalent to equation (6), though with α replaced by $\alpha - \beta_{ax}S_{ax}$ and with β_{ax} replaced by $\beta_{ax} - \alpha S_{ax}$, where S_{ax} is the overlap integral, $\int\phi_a\phi_x d\tau$. All this justifies our belief that, except for very electronegative substituents, the qualitative conclusions of expressions (9) and (10) will not be seriously affected by the inclusion of overlap.

Conclusions.—The simple conclusions to be drawn from this study are: (1) conjugation across a single bond may be measured in terms of delocalisation energy, charge migration, or bond order: the three relevant formulæ show a close similarity to each other, and in particular the delocalisation-energy and bond-order values are almost proportional; (2) in every case the resonance integral is as important as the coulomb term in determining the extent of the additional conjugation; (3) increasing the electronegativity of a substituent X without any change in the resonance integral reduces the degree to which it can conjugate with the initial hydrocarbon; and (4) a proper quantitative understanding of this type of conjugation is quite impossible until more information is available of the way in which the resonance integral between dissimilar atoms depends on the nature and environment of the atoms concerned.

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