416. *Studies of the Localization Theory of Organic Reactions.*
Part II.* The Effects of Substituents.

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The general theory of the effect of structural changes on the chemical reactivity of an aromatic molecule, developed in Part I * for changes corresponding to introduction of hetero-atoms or annelation of other ring systems, is now extended to embrace the effects of substituents. The change in localization energy produced by a substituent is shown to be related to certain conjugation energies of the substituent. The empirical relationships of the conjugation energies to self-atom-polarizabilities are employed to facilitate calculation of the change in localization energy.

The results of the theory are illustrated by a detailed application to 9-phenyl- and 9 : 10-diphenyl-anthracene. It permits a very crude estimation of the average relative orientations of the phenyl and the anthracene systems in these molecules of 20° in boiling xylene. A probable explanation is provided for some apparently contradictory experimental results for the Diels–Alder reactions of these molecules and of 6 : 13-di-phenylpentacene.

It is noted that alkyl substituents are anomalous and cannot be treated by the present theory.

IN Part I * the general theory of the change in reactivity of a conjugated system produced by certain alterations to its structure was developed, on the basis of the localization treatment of reactivities, for structural changes corresponding to the fusion of a second conjugated system to one of the bonds of the first, or to the replacement of one of the atoms of the conjugated system by another atom of different electronegativity. In the present paper this study is extended to embrace the effects of substituents.

Let the original conjugated system, A, have a π-electron energy $\mathbf{E_0}$. The localization energy, $\mathbf{L_0}$, corresponding to some particular reaction of the molecule, and to some particular reactive position (or set of positions) therein, will be given by

$$\mathbf{L_0} = \mathbf{E_0^r} - \mathbf{E_0} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

where $\mathbf{E_0^r}$ is the π-electron energy of the residual molecule appropriate to the reaction and position of attack chosen. $\mathbf{L_0}$ and $\mathbf{E_0^r}$ will of course in general depend upon the position (or set of positions) in the molecule whose change in reactivity is under consideration. If now a substituent X (*e.g.* vinyl-, phenyl-, chloro-, hydroxy-) is attached to position i of the original conjugated system, A, then the π-electron energies of the substituted molecule and substituted residual molecule may be written

$$\mathbf{E} = \mathbf{E_0} - \mathbf{C}_i + \mathbf{E^X} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

$$\mathbf{E^r} = \mathbf{E_0^r} - \mathbf{C}_i^r + \mathbf{E^X} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

$\mathbf{E^X}$ represents the π-electron energy of X, and $\mathbf{C}_i$ and $\mathbf{C}_i^r$ the π-electron conjugation energies of X with the original molecule and residual molecule, respectively. These conjugation energies, as indicated by their subscripts, will in general depend upon the position of attachment, i, in the original and residual molecules.

Clearly, from (1), (2), and (3), the localization energy of the substituted system is given by

$$\mathbf{L} - \mathbf{L_0} = \mathbf{C}_i - \mathbf{C}_i^r \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

while if several different substituents are present, and they may be treated independently (which will frequently be an acceptable approximation), equation (4) is to be replaced by

$$\mathbf{L} - \mathbf{L_0} = \Sigma_i \, (\mathbf{C}_i - \mathbf{C}_i^r) \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (5)$$

the summation being taken over all substituted positions.

* Part I, *J.,* 1951, 1955.

The relationships considered so far are merely identities resulting from definitions of the various π-electron energies concerned. They do not depend upon the assumption of any particular quantum-mechanical approximation for calculating these energies, and in particular they remain valid for both the valence-bond and the molecular-orbital approximations to the energies. To indicate this bold-face symbols have been employed, as in Part I. If, however, we particularize to the molecular-orbital approximations to these energies (which will now be represented by ordinary italicised symbols) it is possible to use certain general results to estimate the relevant conjugation energies. Equation (4) [or (5)] then becomes vastly more convenient for discussing changes in reactivity brought about by the substituent than the direct method of calculating the necessary localization energies of generally rather large conjugated systems. Also it permits us to draw a general conclusion about the qualitative effect of substituents of any kind.

As in Part I we shall consider only the case where the initial conjugated system, A, is an alternant hydrocarbon. It is convenient to consider various types of substituent, X, separately.

(i) *X is an Alternant Hydrocarbon System.*—Conjugation energies of alternant hydro-carbons with one another have been discussed in some detail and equations are available for the computation of C_i directly with relatively high accuracy (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1948, *A*, **195**, 188; de Heer, *Phil. Mag.*, 1950, **41**, 370; Brown, *Austral. J. Sci. Res.*, 1949, *A*, **2**, 564; *idem, ibid.*, in the press). The relationships involve the self-atom-polarizabilities of the two positions in A and X, respectively, through which the conjugation is effected. The self-atom-polarizabilities have been studied only for uncharged molecules with even numbers of π-electrons, so the equations cannot at present be employed to estimate C_i^r if one of the components is a radical or ion. In the case of electrophilic, nucleophilic, and homolytic substitution reactions the residual molecules fall in these latter categories, so the use of equation (4) and the empirical relationships for estimating C_i and C_i^r must at present be restricted to the Diels–Alder reaction and the osmium tetroxide oxidation, for which the residual molecules are uncharged and contain even numbers of π-electrons. However, attempts are being made to obtain conjugation-energy relationships applicable to the other types of residual molecule which arise from consideration of the other organic reactions.

Suppose position x in X is linked to i in A. Then from the explicit expression for the conjugation energy (Brown, *Austral. J. Sci. Res.*, in the press)

$$C_i = -(0.811\sqrt{\lambda_i\lambda_x} + 0.062)\beta \qquad . \quad . \quad . \quad . \quad . \quad (6)$$

or *

$$C'_i = -(0.623\sqrt{\lambda_i\lambda_x} - 0.132)\gamma \qquad . \quad . \quad . \quad . \quad . \quad (7)$$

where λ_i and λ_x are the magnitudes of the self-atom-polarizabilities of position i in A and x in X (in units of $1/\beta$). A similar expression, with λ_i replaced by λ_i^r, results for C_i^r, of course, so (4) may be written

$$L - L_0 = \mu_x(\mu_i^r - \mu_i)\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

or

$$L' - L'_0 = \mu'_x(\mu_i'^r - \mu'_i)\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In these equations we have for convenience written $\mu = 0.901\sqrt{\lambda}$ and $\mu' = 0.789\sqrt{\lambda}$. Numerical values of μ and μ', which may be regarded as conjugating powers, have been tabulated for various positions in a large number of alternant hydrocarbons (Brown, *loc. cit.*).

We may deduce immediately from (8) or (9) that the substituent X increases the reactivity of A when $\mu_i^r > \mu_i$ (*i.e.*, $\lambda_i^r > \lambda_i$), or decreases it if the reverse is the case. In general, however, the change in reactivity predicted by these equations is very small. For example, let us consider the effect of a phenyl substituent in position 1 of anthracene on

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* In conformity with previous usage (*e.g.*, Brown, *Trans. Faraday Soc.*, 1950, **46**, 146), energy quantities for which the overlap integral between nearest neighbours has been included are represented by primed symbols.

the reactivity of the 9 : 10-positions in a Diels–Alder reaction. The relevant numerical data are :

$$\mu_x \text{ (phenyl)} = 0.568 ; \ \mu_i \text{ (1-anthryl)} = 0.607 ; \ \mu_i^r \text{ (phenyl)} = 0.568$$
$$\mu'_x = 0.498 ; \ \mu'_i = 0.532 ; \ \mu''_i = 0.498$$

and we find that :

$$L - L_0 = -0.02_2\beta ; \ L' - L'_0 = -0.01_7\gamma$$

This represents a very small decrease in reactivity of the 9 : 10-positions, corresponding to a theoretical relative rate constant (Brown, *J.*, 1950, 3249) of about 2. For comparison, the difference in localization energies of the 9 : 10-positions and the 1 : 4-positions of naphthalene [which only undergo Diels–Alder addition under forcing conditions (Kloetzel and Herzog, *J. Amer. Chem. Soc.*, 1950, **72**, 1991)] is -0.37β or -0.33γ (Brown, *J.*, 1950, 691).

The change in reactivity of a pair of positions is, however, much greater if X is actually attached to one of them. Then the localization process destroys the conjugation between X and A, and C_i^r thus becomes zero. Consequently, from (4), we deduce that there will be an appreciable decrease in reactivity due to the presence of X. For example, consider the change in Diels–Alder reactivity of the 9 : 10-positions of anthracene arising from a phenyl substituent in the 9-position. From (7) we calculate C'_i to be $-0.15_3\gamma$, and according to (4) this represents $L' - L'_0$. The diminution in the Diels–Alder reactivity of the 9 : 10-positions of anthracene by phenyl substituents in the 9- or 9 : 10-positions has been observed experimentally by Bachmann and Kloetzel (*J. Amer. Chem. Soc.*, 1938, **60**, 481) who measured the equilibrium concentration of the adduct of anthracene, 9-phenyl-anthracene, and 9 : 10-diphenylanthracene with maleic anhydride in boiling xylene. These authors' measurements on related polycyclic hydrocarbons have been shown (Brown, *J.*, 1951, 1612) to be in quantitative agreement with the relevant para-localization energies, P', so the analogous data for the phenylanthracenes should provide a good test of the above theory.

Let us consider first 9-phenylanthracene. If variations in the free energies of reaction arise substantially from variations in para-localization energy, as was assumed in previous theoretical studies of the equilibria (Brown, *loc. cit.*), then the difference between its 9 : 10-para-localization energy and that of unsubstituted anthracene may be written, according to (4) as follows :

$$P' - P'_0 = C'_9 = \Delta G - \Delta G_0 \quad . \quad . \quad . \quad . \quad . \quad (10)$$

From (10) the " experimental " value of C'_9 derived from the observed equilibrium concentrations is $-0.11_8\gamma$ [as in the previous study of equilibria (*loc. cit.*) γ has been taken as $-33._6$ kcal.].

The discrepancy with the theoretical value of $-0.15_3\gamma$ (see above) is greater than could be explained by the various experimental and theoretical uncertainties, but it is easy to see how it arises. The conjugation-energy equations (6) and (7) tacitly assume that X and A are coplanar. A partial rotation about the linking bond would reduce the conjugation energy considerably, and could easily reduce the theoretical value to one equivalent to the " experimental " value.

The variarion of C' with the relative azimuth, ψ, of X and A may be written

$$C'(\psi) = C'(0) . f(\psi) \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Guy (*J. Chim. physique*, 1949, **46**, 469) has made calculations of $f(\psi)$ by a variation method. His equations are rather cumbersome, but his tabulated values are represented very well by the simple function $\cos^5\psi$. The values $-0.15_3\gamma$ and $-0.11_8\gamma$ for $C'(0)$ and $C'(\psi)$, when inserted into (11), consequently correspond to $f(\psi) = 0.77$, *i.e.*, $\psi = 18._5°$.

A similar calculation may be performed for 9 : 10-diphenylanthracene. In this case $C'(0)$, obtained by exact calculation from the complete secular determinant, is -0.3144γ, while the equilibrium concentration found by Bachmann and Kloetzel (*loc. cit.*) leads to $C'(\psi) = -0.20_9\gamma$. These values correspond to an azimuthal angle for the two phenyl groups relative to the anthracene system of $\psi = 22._9°$. The agreement between the

estimates of mean azimuthal angles for these molecules, in both cases for a temperature of about 140° in xylene, is surprisingly good in view of the approximations involved in the calculations. We might, for example, expect the assumption of constancy of ΔS, implicit in the assumption $\Delta(\Delta G_0) = \Delta P'$, to be less satisfactory when flexible substituents are present. It is of interest that Guy, who investigated the sterically rather similar *o*-methyl-diphenyl by a different theoretical method, obtained an energy curve with a minimum around 18°.

In the general case of the change in reactivity produced by substituents, it was shown that the direction of the change in reactivity may immediately be predicted from the relative magnitudes of λ_i^r and λ_i. Likewise if we consider the relative effects of a series of substituents X in one particular position i of A, their effectiveness in changing the reactivity will be in the order of their λ_x. Thus from a table of polarizabilities we may predict that the following groups have a decreasing order of effectiveness :

$$\text{9-anthryl} > \text{vinyl} > \alpha\text{-naphthyl} > \beta\text{-naphthyl} > \text{phenyl} > \ldots \ldots$$
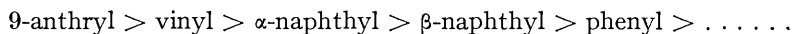
and we could of course include many other hydrocarbon substitutents in this list. Again this order may be complicated by steric effects of the type discussed for the phenyl-anthracenes above.

(ii) *X is a Single Hetero-atom, contributing 2 π-Electrons.*—Substituents such as amino, hydroxy, and halogeno are of this type. Conjugation energies of this type of substituent with an alternant hydrocarbon have been investigated by Coulson and de Heer (*Trans. Faraday Soc.*, 1951, **47**, 681). The hetero-atom of the substituent X is to be characterized by a coulomb integral α_X and a resonance integral β_{CX}, and by writing :

$$\alpha_X - \alpha_0 = h \cdot \beta\,; \quad \beta_{CX} = k \cdot \beta_{CO} = k \cdot \beta$$

these authors derived the relation

$$C_i = -0 \cdot 67 k^2 (\lambda_i/h)^{1/2} \beta \qquad \ldots \ldots \ldots (12)$$

In this case therefore (4) becomes

$$L - L_0 = (\text{const.}) k^2 \beta (\mu_i^r - \mu_i)/\sqrt{h} \qquad \ldots \ldots \ldots (13)$$

We may note in passing that the numerical constant $0 \cdot 67$ in (12) was obtained only for X = OH, and may be quite different, but necessarily still positive, for other substituents. For this reason the numerical constant in (13) has not been given explicitly.
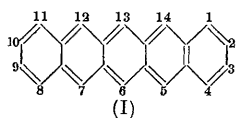
We see again that the change in reactivity is governed by the relative magnitudes of λ_i^r and λ_i, so that qualitatively we need make no distinction between the effects of substituents of class (i) and class (ii). Again we expect the effect to be small unless X is attached to one of the positions undergoing reaction.

This latter effect is illustrated experimentally by the decreased Diels–Alder reactivity of 9-bromoanthracene compared with anthracene (Bachmann and Kloetzel, *J. Org. Chem.*, 1938, **3**, 55). Equation (13) also explains the observation (Badger and Lynn, *J.*, 1950, 1726) that 10-bromobenzanthracene reacts more slowly with osmium tetroxide than does the parent hydrocarbon. In this example λ_i is the polarizability magnitude of the 10-position of benzanthracene (0·514), while for the residual molecule λ_i^r is the polarizability magnitude of the 4-position of 2-phenylnaphthalene. The latter is doubtless very similar to that of the 4-position in naphthalene itself, *i.e.*, 0·443, and so certainly less than λ_i. Hence the relative magnitudes of λ_i and λ_i^r are in agreement with the slightly decreased reactivity of the bromo-compound observed experimentally.

(iii) *X is Polyatomic and containing Hetero-atoms.*—The most important groups of this class are probably carboxy, nitro, cyano, and formyl. The conjugation energies of such groups have not been investigated explicitly, but they too doubtless depend upon λ_i and λ_i^r in the same way as for the substituents previously discussed.

(iv) *X is an Alkyl Group.*—This type of substituent shows some interesting anomalies when the present theory is applied to explain relevant experimental data, particularly for the Diels–Alder reaction. It is hoped to consider such substituents in detail in a subsequent paper.

Now since substituents attached to the most reactive pair of positions appreciably reduce its reactivity but have little effect on the reactivities of other pairs, it may be possible to obtain addition of a dienophile at a pair of positions in the substituted hydrocarbon which cannot be made to undergo addition in the parent hydrocarbon. Pentacene (I) provides an example of this. The unsubstituted molecule is most reactive in the 6 : 13-positions (Clar, *Ber.*, 1931, **64**, 2194), but 6 : 13-diphenylpentacene undergoes addition at the 6 : 13- and 5 : 14-positions in nearly equimolar quantities * (Allen and Bell, *J. Amer. Chem. Soc.*, 1942, **64**, 1253). This might have been expected theoretically because the para-localization energies of the 6 : 13- and the 5 : 14-positions of pentacene itself do not differ very greatly ($\Delta P' = -0.05\gamma$; Brown, *J.*, 1950, 691).

In anthracene the difference in reactivity of the 9 : 10- and 1 : 4-positions is much greater ($\Delta P' = -0.27\gamma$) than this. Indeed by using the theoretical para-localization energies to predict equilibria it is found that under the conditions employed by Bachmann and Kloetzel (*locc. cit.*) the 1 : 4-positions, reacting alone, would provide only 3% adduct at equilibrium, but the 9 : 10-positions alone would produce 98% of adduct at equilibrium. Further, when the two phenyl groups are coplanar with the anthracene system, so that their deactivating effect is a maximum, the value of P' for the 9 : 10-positions of diphenylanthracene is -2.3888γ, virtually the same as for the 1 : 4-positions (*i.e.*, -2.3872γ). We should expect from this that for all values of ψ the addition will occur chiefly at the 9 : 10-positions. Again we may calculate that in 9 : 10-diphenylanthracene the 1 : 4-positions acting alone would provide only 0.3% of adduct under Bachmann and Kloetzel's conditions (assuming coplanarity of the substituents with the anthracene system). Since Bachmann and Kloetzel found that diphenylanthracene yielded 16% of adduct, this may be reconciled with the theoretical results summarized above only if the addition occurred almost entirely at the 9 : 10-positions. This also would have been expected from the observations on pentacene discussed above.

Gillet (*Compt. rend.*, 1948, **227**, 853; *Bull. Soc. chim.*, 1950, **17**, 1141), however, found spectrophotometrically that the addition to 9 : 10-diphenylanthracene was exclusively at the 1 : 4-positions. This is hard to reconcile with the above results, although an examination of the conditions employed to form the adducts suggests a possible explanation. Bachmann and Kloetzel and Allen and Bell studied the additions in boiling xylene (*i.e.*, about 140°). Gillet reported that for diphenylanthracene the reactants were recovered unchanged in boiling xylene (cf. isolation of 16% of adduct under these conditions by Bachmann and Kloetzel), and prepared the adduct by fusing diphenylanthracene with maleic anhydride at 200°. This suggests that at the higher temperature the phenyl substituents vibrate more violently about their linking bonds so that 9 : 10-addition is prevented by steric hindrance, while at 140° this effect is no longer sufficient to prevent addition at these positions. This interpretation of course could easily be tested experimentally by repeating Bachmann and Kloetzel's work and examining the structure of their adduct spectrophotometrically, and also it might prove possible to suppress entirely addition at the 6 : 13-positions of the sterically similar diphenylpentacene by carrying out the reaction at higher temperatures. Clearly a more detailed study of these and other phenyl substituted polycyclic compounds is called for.

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* The adduct at the 5 : 14-positions of course undergoes a second addition at the 7 : 12-positions since it contains a conjugated system equivalent to 1 : 4-diphenylanthracene.

7 D