THE SUBSTITUTION OF LINKED AROMATIC RING SYSTEMS

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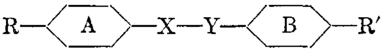
General interest in the experimental investigation of the substitution reactions of chemical molecules containing more than one aromatic ring system may be traced back to 1912, when Cain, Coulthard and Micklethwait (1) announced that two distinct dinitrobenzidines could be obtained by nitrating acyl derivatives of benzidine. By analogy with the known reactions of aniline, there should have been produced, instead of these two isomers, but one substance—3, 3′-dinitrobenzidine. Unfortunately, the correct elucidation of this discovery was delayed for several years, owing to the proposal of a stereochemical explanation of the isomerism which, though incorrect, served to divert attention from the actual question of the mode of substitution of more complex aromatic compounds.

Since 1920, however, the very rapidly increasing number of experimental studies has shown clearly that the early empirical rules for the classification of substitution-directing groups—such as that of Crum Brown and Gibson—are inadequate guides for the prediction of the courses of substitution reactions. Also, following the application of the newer electronic theories of valency to organic chemistry, it has been realized that the explanatory theories of aromatic substitution must be based essentially upon experimental facts of unquestionable validity and not upon deductions based on analogies and statistical schemes of correlations. Consequently the field of investigation has been widened, and the substitution reactions of such complex aromatic compounds as diphenyl, benzophenone, phenylpyridine, and other substances containing more than one aromatic ring linked up within a single molecule, have become worth experimental study.

Though the as yet recorded observations of the substitution reactions of compounds having the general type of figure (I), in which two *independently complete* aromatic rings (A) and (B)



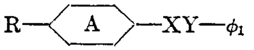
(I)

are linked together by any grouping or assemblage of groupings (−XY−), are very scattered and incomplete, they have already attracted considerable attention in one or two instances, notably in the cases of the diphenyl and phenylpyridine series. It should be noted that only with compounds of type (I) is it possible to ensure that comparisons of the reactivities of the two different aromatic nuclei (A and B) are made under absolutely identical experimental conditions. Whatever types of reactions are carried out with such "binuclear" substances as these, both rings must remain equally affected by the many possible external influences, such as those due to the substituting reagent, to the solvents employed, or to the catalysts which may be present. No such certain elimination of differential external effects, which might arise through mere differences in solubility or in degree of solvation, can be attained when two different aromatic molecules are compared, even if these are mixed together before treatment with a common substituting reagent, as has been done in several recent researches (2, 3).

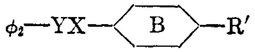
It is the object of this article to correlate the experimental results recorded throughout the whole wide field of investigation outlined above, and to discuss their general characteristics in terms current in modern theories of aromatic substitution.

Several different characteristics of aromatic substitution can be studied with the aid of linked ring systems, according to the actual types of compounds chosen for investigation. With simple compounds like diphenyl, or benzophenone, one can examine first the degree of reactivity and the mode of direction of substituting groups in any one ring (A) produced by the other ring (B), acting of course in combination with the linking group (−XY−). When this linking group is unsymmetrical—as in benzoin—it will induce different reactivity effects in the two rings. These can be differentiated from each other and compared directly with great ease. Consequently one can study the effect of systematic variation of any divalent group (−XY−).

In more highly substituted linked ring compounds, of the type actually formulated in figure (I), further effects due to the other substituent groups (−R) and (−R′) can be traced. The compound (I) can be analyzed as if made up of two substances (II) and (III),



(II)



(III)

each containing an aromatic ring in which substituent groups may compete in controlling the mode of substitution. Since any substance of type (I) may also be regarded as a substituted linked ring compound, it may be anticipated that valuable results may be obtained by studying the reactions of highly substituted aromatic compounds.

In all "linked ring systems" effects may be traced which are due not only to the special properties of the substituent groups (R and R′) or linking groups (X and Y), but also to the ring systems (A and B) themselves. Reactivity in ring (B) may be induced or inhibited by special influences from the aromatic ring (A) that are transmitted either through space or through the linking groups, and comparisons may be made of the relative actions of the various linking groups (−XY−) in assisting or in hindering this transmission.

Linked ring systems can therefore provide data for the systematic comparison of several of the more important factors influencing aromatic substitution.

Modern explanations of aromatic substitution, even when applied to the simplest of benzene derivatives, all involve the recognition of at least two distinct electropolar influences, apart from the possibility of the intervention of the geometrical effect known as "steric hindrance". Dual substitution influences can also be discerned in all these more complex compounds, so that before one can proceed to the explanation of experimental results, it is necessary to differentiate between these polar influences and to trace their separate characteristic manifestations within aromatic rings.

It was first pointed out by Hollemann (4) that the speeds of substitution of different aromatic compounds were markedly different; substances containing *ortho-para* directing groups being more reactive and those containing *meta* directing groups less reactive than benzene itself. This effect has now been recognized definitely as a *general polar action* of the substituent group which is exerted through space and through the intervening atoms in the molecule. Its magnitude can be evaluated in terms of the energy required for ionization at any point of reaction under particular consideration, for a substituent group within any molecule will, in general, modify the electrostatic environment of possible reactive atoms by inducing a definite change in the local electrical potential. By estimating this induced electrical potential in terms of the magnitude of the electrical dipole moment of the directing group, it is possible to get a rough basis of measurement of this general polar effect (5). As Ingold has pointed out (6, 7), this induced electrical polarity may be exerted directly across space, and also relayed successively from atom to atom within the molecule. In certain special cases he has found it advisable to differentiate between these two modes of action, and has named their resultant manifestations the "direct effect" and the inductive effect," respectively. Usually, however, only the resultant sum of these two general polarization effects need be taken into consideration for the explanation of experimental observations.

It is probable that the realization that there can be these two distinct modes of propagation of the "covalency adjustments" of the general polarization effect will attain much significance in the future development of this subject, for, to quote a recent statement by Lapworth (45) in discussing the theory of induced polarization—"Insufficient attention has been paid to the possibility, already partly recognized, that even in the resting state of a molecule the effect of a substituent at a given point, even at a considerable distance from the substituent, may be the resultant of at least two simultaneous influences, one reaching the point from the exterior and the other from the interior, that is *via* the electronic system of the adjacent atom, the condition of which, in its turn, is likely to be determined by the resultant of interior and exterior influences. The exterior and interior forces at a given point may operate either in harmony or in opposition according to the nature of the substituent, and possibly also according to other circumstances, and obviously may affect one another to a greater or less extent throughout the whole range of collateral transmission."

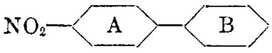
Theoretical conceptions of the nature of all polarization effects vary very widely, but, whatever conceptual scheme be adopted, there is no doubt at the present time that the *general* polarization effect can be termed an *inductive disturbance.*

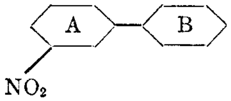
General polar influences, primarily altering speeds of reaction, cannot however be used adequately to explain the attraction of entering substituting groups to special points of potential attack in the aromatic molecule. It has been necessary therefore to postulate the existence of an alternating polarity effect, superposed upon the general polarization effect. According to all theories this is regarded as an influence emanating from the "directing substituent group" inducing special reactivity, at the moment of substitution if at no other time, in either the *ortho* and the *para,* or else in the *meta* positions within the same aromatic ring. Recent experimental work (10, 11) seems to indicate that this alternating polar influence can rarely be exerted from outside a single aromatic ring. The effect is probably best considered as an induced tautomeric (or rather electromeric) disturbance (8, 9).

Whatever detailed explanatory schemes be utilized for the description of these two types of induced polar influences, their intrinsic natures can be sharply differentiated as outlined briefly above. The standard nomenclature of Ingold (6, 8, 9) for these effects will therefore be employed throughout the rest of this article, the general polarization effect being denoted by *I*, and the alternating polarity effect by *T*. Except where specifically stated, the general polarization effect, as denoted by *I*, will be taken as including also the direct effect *D*.

Evidence obtained from the recorded substitution reactions of linked ring systems, when examined from the modern electronic viewpoint as outlined above, indicates that aromatic rings do very distinctly exert specific inherent polar influences. In brief it may be stated that, though aromatic rings readily permit the transmission of induced electronic movements, involving both the acceptance and the donation of electrons, yet, as far as their own influences are concerned, one consistent type of polar action is to be observed. The aromatic ring therefore does not act merely as a resonator to influences arising elsewhere but also induces electron movements on its own account.

This has been recognized most clearly in the case of the diphenyl ring system, which has been investigated very thoroughly during the past few years (11–15, 36, 40). Although all diphenyl derivatives are completely conjugated systems, in which electromeric polarity transmission (*T*) might easily occur from ring to ring, yet experiment has shown that not only the unsubstituted phenyl group (C_6H_5) but also *all* substituted phenyl groups (C_6H_4X) have one consistent type of directive action, which is similar to that of all other hydrocarbon radicals (11, 12, 13, 15). Thus, on substitution of all three nitrodiphenyls (figures IV-VI)


(IV)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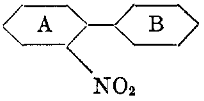
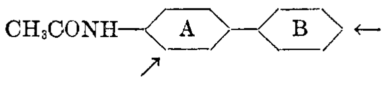

(VI)

the entering groups invariably attack positions in ring (B) in the *ortho-para* relationship to the nitrophenyl group (A). The same can be stated for substitution in ring (B) when even more powerful orienting groups, like $-NH_2$ or $-OH$, are present in ring (A) (12, 13, 14). Only when the aromatic ring undergoing substitution already contains another substituent group, more powerful in its directive influence than the substituted phenyl group linked to it, can reaction occur at positions in the *meta* relationship to the bond linking the two aromatic nuclei. This is well illustrated by reference to the acetamidodiphenyls (VII) and (VIII) in which substitution can occur, according to the special experimental conditions, in either of the two nuclei at the positions indicated (12, 14).



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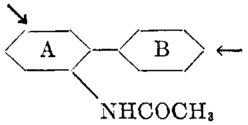
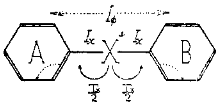


(VIII)

Examination of all other linked ring systems reveals a similar consistency of type of directive action, unaffected by the presence of substituent groups in the ring not actually being substituted.

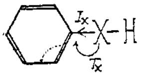


(IX)

In any compound $C_6H_5-X-C_6H_5$ (figure IX) it is usually impossible for induced alternating electron pulses to be propagated from one ring to another through the linking group $(-X-)$, for, in general, linking groups are not conjugated systems which can undergo the requisite type of electromeric transformation (*T*) consistent with the preservation of stable electronic groups around each atom. Even in completely conjugated compounds in which internuclear electron movements can and do occur (as, for example, in the case of the cyanine dyestuffs), the alternating polarity influence does not seem to be powerful between the two rings.

Internuclear directive effects have certainly been detected in such compounds as the phenylpyridines (16) though they are not strongly marked, while in such homocyclic systems as diphenyl and azobenzene (17) they have not been found. There may perhaps be an intrinsic difference in the amount of energy required for the sporadic electromeric disturbances (*T*) which influence reactivity and for those regular, and exceedingly rapid, intramolecular electronic movements to which correspond those absorption band spectra which are so characteristic of all aromatic substances.

In contrast to the restricted range of the alternating polarity influence, general induced electron drifts (I) can be exerted from ring to ring, as they are transmitted, in part at least, through space, and so can only be partly suppressed by the intervening group (–X–). The resultant reactivity of any one ring in a compound (IX) will therefore be influenced by the total $(I + T)_x$ polarization induced by the group (–X–) plus that proportion of the induced electron drift due to the other ring ($I\phi$) which is transmitted through the linking group. The alternating polarization influence (T_x) exerted by the linking group (–X–), however, will be distributed between the two rings (A) and (B), and therefore will have a markedly different magnitude in either from what it would have in such a compound as figure (X), in which tautomeric electron movement can proceed from (–X–) in one direction only.



(X)

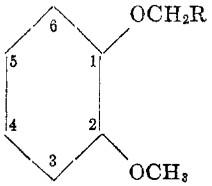
The general "electron drift" polarization (I_x), induced by the linking group (–X–), if of the nature of an induced electrical potential as has been suggested, will not be so markedly different in the two substances (IX) and (*X*), for that portion of it which has been characterized as the direct effect (D) should certainly be induced equally on free space or on distant atoms, while the other fraction, transmitted from one atom to the next, should diminish in intensity only with the length of the chain of atoms involved.

When these possibilities of induced polarization are fully taken into account it is found, from collected experimental data, that in all linked ring systems the phenyl group acts uniformly as a powerful "electron source" group with a directive action similar in type to that of the hydrogen atom. It generally increases reactivity (+*I*), and, when it can originate an activating electromeric disturbance, always induces substitution in the *ortho* and *para* positions in another ring (+*T*). It thus resembles any other hydrocarbon radical, as, for example, the methyl group $-CH_3$ (18).

In illustration of this conclusion it may be pointed out that similar substitution reactions are given by all compounds in any related series ($\phi-X-R$), in which the group ($-R$) may be a hydrogen atom (as in (X)), an alkyl group, or an aryl group (as in (IX)). For example, benzophenone, acetophenone and benzaldehyde are all relatively inert, *meta* substituting compounds, the outer group $-R$ being unable to influence the reacting ring through the intervening carbonyl group. Diphenyl ether, anisole and phenol in contrast are all *ortho-para* substituting compounds with reactivities differing only in degree according to the extent to which the outer group $-R$ limits the frequency of the activation due to the oxygen atom.

The polar effects due to the outer group ($-R$) are in all cases very slight, but they can be detected quite distinctly by quantitative measurements of directive powers. In such quantitative experiments as have already been carried out it has been demonstrated that an aromatic ring has, in a compound of type (IX), an activating influence (+*I*) of a magnitude very similar to that of the methyl group in an analogous compound of the same general type $\phi-X-R$.

Allan and Robinson (19), for example, have examined the nitration of a series of guaiacol ethers of the type of figure (XI), all of which substitute exclusively in the positions 4 and 5—i.e. in the *para* positions to the groups $-O-CH_2-R$ and $-OCH_3$ respectively.



(XI)

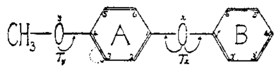
From the equation:

$$\frac{\text{Directive power of } —\text{OCH}_2\text{R}}{\text{Directive power of } —\text{OCH}_3} = \frac{\text{per cent of 4 substitution}}{\text{per cent of 5 substitution}}$$

they have been able to obtain fairly accurate estimates of the magnitude of the general polar influence (*I*) of the group ($-$R) in modifying the polarization of the oxygen atom of the ether linkage, through which the reactivity is eventually induced. Relative to the directive power of the methoxy group (R = H) being taken as 100, the directive powers of the methoxy group (R = CH_3) and of the benzyloxy group (R = C_6H_5) are respectively 135 and 113. Replacement of the phenyl group by the methyl group, or by hydrogen, has therefore but little effect on the magnitude of the resultant induced polar influence (*I*) which is transmitted through the linking group $-OCH_2-$. A similar comparability between the *ortho* directive powers of alkyl and aryl groups has been found in analogous types of ethers of the quinol series (20).

This similarity of action of alkyl and aryl radicals applies, however, only to the consideration of general polarization effects (*I*) induced by aromatic rings on atoms exterior to them. It is not in accordance with the experimental facts relating to all types of linked ring systems. For example, on comparing compounds of linked ring systems with those containing only one ring system (e.g. X) it has been found that the special activation induced by the alternating polarization mechanism (*T*) is appreciably less in the case of the compound with the linked ring systems (e.g. IX). This difference arises because there is a distribution between the two rings (A) and (B) of the alternating polarity effect originated by the linking group ($-$X$-$). The tautomeric electron pulses (*T*), which produce either *ortho-para* or else *meta* substitution as the case may be, are usually considered to occur only in momentarily activated molecules. An activating group (in this case $-$X$-$) can be assumed to receive extra (? quantized) energy, or perhaps an extra electron—possibly from an external catalyst or as the result of an intermolecular collision—and to hand on this energy, or electron, very rapidly, by the tautomeric process, to the actual point at which substitution occurs. One momentary production of an activated grouping in any individual molecule will result in the activation of one point only of potential substitution, and, in the case of a linked ring compound, this may be produced, through the (*T*) process, in either of the two rings. As the measurable rate of substitution will depend primarily upon the frequency of activation of the directive grouping, and only secondarily upon the course of the tautomeric change subsequently resulting, the chance of resultant activity appearing at any one point of potential substitution in a large conjugated system, such as a molecule with linked aromatic rings, is less than in a more restricted system, such as a molecule containing only one aromatic nucleus. This can best be illustrated by the following reference to experimental fact.

While investigations of the substitution reactions of various methylbenzyl ethers of the catechol and quinol series (see p. 415) showed that the benzyloxy and methoxy groups had comparable directive powers, investigations of the phenyl methyl ether of quinol (XII) showed that substitution occurred exclusively in position 3 in ring (A) (21).



(XII)

The occasional electron pulse activation of the oxygen atom (x), transmitted intermittently to one or other of the two rings is no longer comparable, in ring (A), with the unidirectional activation of the oxygen atom (y) of the methoxy group. This latter group can therefore control the actual mode of substitution in the whole molecule.

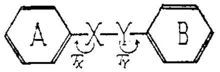
There indeed seems to be a tendency for aromatic nuclei to attract to themselves electrons which may be emitted from any adjacent electron source group (22, 23). Support for this view, though drawn mainly from such evidence as the stability of triphenylmethyl and the reactions of conjugated tautomeric systems, is not lacking within the sphere of aromatic substitution. Apart from the case of diphenyl ether, considered above, it is well illustrated by the inactivity of benzophenone as compared with acetophenone, and of benzoyl derivatives generally in comparison with the corresponding acetyl derivatives. In these cases the difference in activity between similar types of compounds may be expressed through the scheme of Cooper and Ingold (24), according to which decrease in the reactivity of carbonyl compounds corresponds to withdrawal of electrons from the carbon atom of the carbonyl group with consequent increase in the magnitude of the deactivating influence of the $>C=O$ dipole.

As regards its action on any outer substituent group, an aryl radical may be said to diminish the alternating induced polarity of any neighboring group by withdrawing some of the momentary activating electron surges to itself. At the same time it must be regarded as increasing the general reactivity at the more distant parts of the molecule. On the basis of Ingold's classification, the phenyl group is thus to be regarded as of the type $(+I\ -T)$ when *not* acting as the primary electron source in controlling substitution.

When exerting its inherent directive influence, however, the phenyl group has a most pronounced "electron source" character $(+T)$, for it is a strong *ortho-para* directing group. In the substitution of diphenyl, for example, there is no evidence of the formation of *any* meta derivative, whereas the corresponding system with an alkyl directing group—toluene—may yield as much as four per cent of *meta* derivative on substitution. The negative alternating inductive property of the phenyl group $(-T)$ must therefore be regarded as a secondary effect, originating outside the aromatic nucleus, and not as one of its inherent electronic influences.

This characterization of the essential natures of aromatic polar properties is in full accord with the normal modern conception of aromatic substances being essentially freely mobile tautomeric systems, which yet preserve as a whole one distinct resultant electronic configuration.

More complex linked ring compounds, of the type (XIII), having widely separated aromatic nuclei, in contrast to those previously considered, show only the normal polar influences of their constituent parts (A), (B), (X), and (Y).

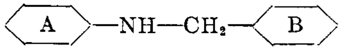


(XIII)

The special interaction of (X) on ring (A) does not affect ring (B), nor does the interaction of (Y) on ring (B) affect ring (A), for electron pulse transmission is rarely possible between the groups (X) and (Y). It is in these compounds therefore that the similarity between the activating properties of alkyl and aryl radicals is most clearly shown, as in the case of the phenyl benzyl ethers to which reference has already been made (p. 415).

Substances containing linking groups such as $-CH{=}CH-$ or $-N{=}N-$, which would complete the conjugation between the two aromatic nuclei, have been but little investigated. They undergo ethylenic addition reactions rather than aromatic substitution reactions but, in a case where the latter is possible (azobenzene), the normal independence of action of the two aromatic rings has been observed (17, 28).

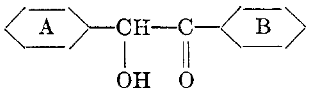
With compounds of type (XIII) it is possible to obtain true comparisons of the relative directive properties of the divalent linking groups (X) and (Y), for (X) will activate atoms in ring (A), and (Y) atoms in ring (B) to extents directly proportional to their intrinsic polar powers (T_x and T_y) alone. External influences, such as those due to solvents, will affect both rings equally, though local "solvation" or "electrostriction" effects (25, 26, 27) due to either of the groups (X) or (Y) may be found. For example the well-known effect of concentrated sulfuric acid in rendering an aromatic base an inert, *meta* substituting substance (for which $-N^{+}\colon H_3$ has $-I\ -T$) instead of a reactive, *ortho-para* substituting substance (for which $-NH_2$ has $+I\ +T$) has been parallelled in linked ring compounds.



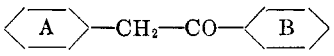
(XIV)

Benzylaniline (XIV) normally substitutes with great ease in ring (A), but its sulfate, in concentrated sulfuric acid solution, nitrates exclusively in ring (B) and yields over 65 per cent of the *meta*-nitro derivative (29). A recent study of the nitration of benzylideneaniline affords another example of the same effect (46). Solvation effects, however, must be regarded as inherent electrochemical properties of these groups, as they arise locally by virtue of the external electrical fields invariably associated with them.

Unfortunately, few comparative data can be deduced from the very slight amount of experimental work which has been carried out with ring systems of type (XIII) up to the present, but, as giving examples of the type of results to be anticipated, the benzoin group of compounds can be briefly considered.



(XV)



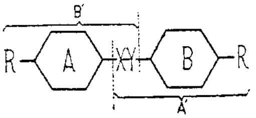
(XVI)

In both benzoin (XV) and desoxybenzoin (XVI), the ring (A) is the one first attacked, and reaction occurs in the *ortho* and *para* positions to the neighboring activating ($+I$ $+T$) linking group (CHOH or CH_2). On disubstitution, after the insertion of a deactivating group (e.g., NO_2) into ring (A), the other ring (B) may be attacked also, and in it substitution occurs in the *meta* position, subject to the polar influence ($-I$ $-T$) of the neighboring carbonyl group. Unlike benzil however, benzoin does give some 4,4′- disubstituted product (30) indicating that the general activating influence ($+I$) of the $-$CHOH$-$ group, adjacent to ring (A), has an actual, though very slight, effect on the more distant ring (B′).

No experimental data, unfortunately, are yet available for compounds of type (XIII) in which the linking groups are of comparable directive powers and with which mixed products should be obtained on substitution.

In order to complete the survey of the substitution of linked ring systems, the properties of already substituted linked ring compounds must now be considered in detail.

As has already been stated (p. 412) it is apparent from experimental work that, in any substance of the general type of figure (I) or of figure (XVII), the type of substitution reaction induced in any one ring (A) by any other ring system (A′) linked to it is, in every case, constant, no matter what substituent groups (R′), other than linking groups ($-XY-$), may be present in the ring (B) which may affect its own internal substitution reactions. Thus, in the benzophenone series, a substituted benzoyl group ($-CO-C_6H_4R$) *always* has a deactivating ($-I$), *meta* directing ($-T$) influence, whatever the nature of the group ($-R$) (31, 32, 33). Similarly, in the diphenyl ether series a substituted phenoxy group ($-O-C_6H_4R$) always has an activating ($+I$), *ortho-para* directing ($+T$) influence (21, 34, 35, 47).



(XVII)

In the diphenyl series, in which alternate polarity electron pulses could conceivably be transmitted from ring to ring, this constancy of type of substitution product has been demonstrated most conclusively by recent experimental work (11–15). The statement of Vorländer (18) that the substituted benzene ring always preserves its characteristic *ortho-para* directive influence has been firmly upheld, the substituent groups ($-R$) have definitely been shown to have only a secondary influence on the directing effect of one ring on the other, and some investigators have gone so far as to state that any one ring is not at all influenced by modification of the other (11). Though this last sweeping generalization is not absolutely correct (15, 36), there is no doubt that this consistency of *type* of directive action of any ring system has now been proved beyond question. Even in the three isomeric phenylpyridine systems ($C_6H_5-C_5H_4N$), in which the great readiness of the pyridine ring to undergo tautomeric change has specially favored the transmission of alternating polarity effects, this same constancy of type of action is generally preserved (16), and the same rule seems to apply to other linked aromatic-heterocyclic compounds containing two rings both of aromatic character (18, 37, 38, 48). The very strong *meta* directing influence of the nitrogen atoms acting as "positive poles" within the heterocyclic ring is never greater than the general *ortho-para* directive influence of the whole ring system.

This is exactly what one would anticipate on the basis of the modern conception of the nature of the alternating polar influence, for even a very occasional activating electron pulse ($+T$), that could cause a molecule to react, is bound to predominate over any deactivating effect ($-T$) which would not result in the occurrence of substitution.

The accumulation of deactivating influences ($-I$) in a completely conjugated radical may however, by attracting away electrons, bring about the obliteration of electron expelling ($+T$) tautomeric changes, or rather, may cause them to be reversed in direction. As an instance of this, it has been shown that 2-phenylglyoxaline-4,5-dicarboxylic acid nitrates mainly in the *meta* position in the benzene ring, while the unsubstituted phenylglyoxalines nitrate mainly in the *ortho* and *para* positions in the benzene ring (39).

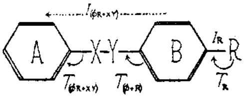
The fact that, for any compound of type (XVII), the position of attack in ring (B) is independent of the *position* of the substituent group (–R) in ring (A) again might be deduced from the electron pulse conception of directive action, though not from all of the earlier theories of alternating polarity.

Once an activating electromeric change brings about the introduction of a new electron into an aromatic ring, then *ortho* or *para* substitution must result, no matter where the original electron source may have been situated in the directing group. Similarly, any abstraction of electrons from an aromatic ring to an outer "electron sink" must render impossible attack by an electropositive substituting ion in these same positions (8, 9). It is the direction of the electronic movement and not its origin which can be correlated with the subsequent substitution reaction.

However, the more important experimental fact that, in addition, the polar nature of the group (–R) (whether an "electron source" like $-OH$, or an "electron sink" like $-NO_2$) is unable to alter the type of directive action of ring (A) can only be explained through inferring that the alternating polar influence (T) cannot be transmitted from ring to ring. Here, on general considerations, it would have been anticipated that internuclear electron transmission might have been possible in certain cases, particularly in fully conjugated compounds such as diphenyl, stilbene or azobenzene derivatives.

Both aromatic ring systems, with mobile electrons which of their own induce "electron source polarization" ($+T$), and the linking groups, which are not usually potential electromeric systems, must act as almost complete bars to the transmission of those electron pulses which are so very powerful within a single aromatic nucleus. One may suggest that this inability of an aromatic ring to transmit an electromeric polarizing influence to another ring is possibly due to its tendency to attract to itself, and to retain, extra electrons (22, 23). See p. 417.

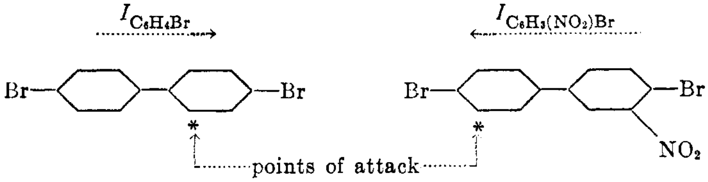
More detailed examination of substitution reactions in linked ring systems, however, reveals the equally important fact that, though the general type of directive influence of any ring system is preserved unchanged on substitution, the magnitude of this directive effect is distinctly affected by the presence of the substituent group.



(XVIII)

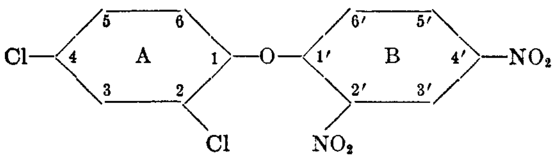
Therefore, though the alternate electron pulse activation (T_R) (figure XVIII) of the group ($-R$) in the ring (B) is unable to reach ring (A), the general electron drift influence (I_R) can be transmitted through the linking group ($-XY-$), in spite of the fact that, in most cases, the linking group exerts a damping effect upon the electron transmission, seriously diminishing its resultant intensity. This experimentally demonstrated conclusion illustrates perhaps the clearest of all the distinctions between the intrinsic natures of the general inductive (*I*) and the alternating tautomeric (*T*) induced polarization influences.

The transmission of the general electronic drift influence of a group ($-$R) to a distant ring has been demonstrated most clearly in the diphenyl ring system, in which there is no linking group that might reduce the magnitude of the resultant induced electrical potential. Many experiments have shown that the inhibiting electron drift ($-I$) due to the presence of a nitro group, and to a less extent also due to the presence of a halogen atom, exerts its influence throughout the whole of the complex system by decreasing generally the rate of chemical reaction in both rings (12–15). It is the action of this general polar influence that results in the unsymmetrical substitution of diphenyl derivatives that has been the subject of so much experimental investigation since the year 1912 (1, 14, 15). It has been shown, for example, that though a chlorophenyl (ClC_6H_4-) or a bromophenyl (BrC_6H_4-) group has a more powerful directive influence than the corresponding halogen atom, yet the introduction of a nitro group into either renders the substituted aromatic ring ($HalC_6H_3NO_2-$) less strongly directing than the halogen atom, on account of the inhibiting electronic drift ($-I_{NO_2}$) initiated by the presence of the nitro group (40, 15, 49) (figure XIX).



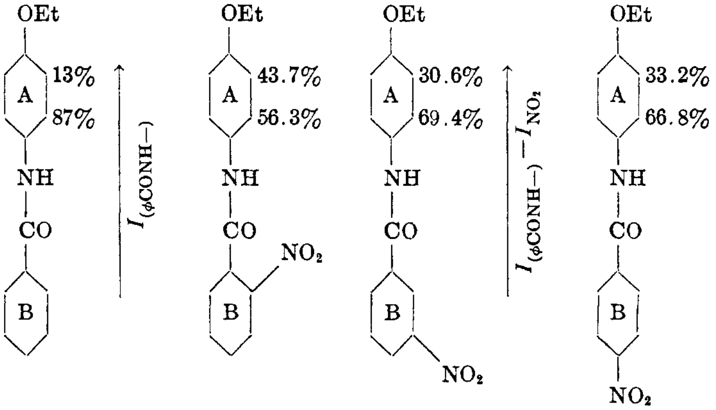
(XIX)

A similar explanation (41, 11) has been given for the formation of the isomeric dinitrobenzidines and dinitrotolidines of Cain (1), which were originally thought to have been stereoisomers and not structurally different compounds. Similar effects have also been observed in the diphenyl ether, phenyl benzoate and phenylbenzene sulfonate series (34, 50). For example 2,4-dichloro-2′,4′-dinitrodiphenyl ether nitrates in position 5 in ring (A) (figure XX) and not in position 6 as would otherwise be anticipated.



(XX)

Further proofs, of more convincing nature, of the existence of this internuclear transmission of the general polarizing influence (*I*) have been given in several recent quantitative researches of Robinson and his colleagues. For example, in continuation of the investigations on the relative directive powers of the groups present in benzylguaiacol, to which reference has already been made (see p. 415), Oxford and Robinson have shown that while the directive power of the benzyloxy group towards its *para* position has a magnitude of 113, relative to that of the methoxy group as 100, the nitrobenzyloxy group has a relative directive power of magnitude only 67, and the chlorobenzyloxy group one of only 82 (42). In both cases the magnitude of this general polar effect is practically independent of the position of the substituent group (NO_2 or Cl) within the directing benzyloxy group. The same effect has also been found among substituted benzamide derivatives (43), and the results may be indicated diagrammatically as in figure (XXI).



(XXI)

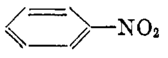
Thus even such a complex and highly polar linking as the $-NH-CO-$ group is unable to block completely the transmission to ring (A) of the electron drift induced by the nitro grouping in ring (B). The experimental results show too that the electron pulse effect (T) of the nitro group is scarcely noticed in ring (A), as the resultant activity in that ring due to the substituted benzamido group is practically independent of the position of the nitro group in ring (B).

That linking groups exert a damping effect upon the transmission of general induced polar effects from ring to ring, however, may be seen from the examination of many substitution results. For example, the very powerful activating groups $-OH$ and $-NH_2$ are unable to induce any appreciable reactivity in the more distant ring in derivatives of both the benzophenone and the azobenzene series (17, 31, 33), though the linking groups concerned ($-CO-$ and $-N{=}N-$) differ very markedly from each other with respect to their own polar influences.

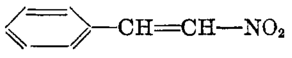
These "damping effects" of the linking groupings may be traced to two distinct sources. Firstly, the linking group, merely by separating the two rings, increases the distance over which the polar influence must be exerted, and so diminishes the magnitude of the resultant induced electrical potential. Secondly, most linking groups contain atoms of polar character which both act as "electron shields" to the original induced electrical potential, and also induce new electronic drifts on their own account, frequently far more potent in magnitude. The importance of the distance factor in hindering the transmission of electronic drifts may be gauged by comparing the substitution results in the diphenyl series with those in the diphenylmethane and diphenylethane series. In the diphenyl series the substituent groups in one ring are occasionally powerful enough to induce unsymmetrical substitution (see p. 424), but in the diphenylmethane and diphenylethane series no such effects have yet been observed, although similar types of compounds have been investigated (44).

The polar action of the linking group, however, contributes most to the prevention of electronic drifts through long chains of atoms. For example, in all qualitative experiments, the benzophenone system, containing a strong partial dipole group ($\overset{+}{C}=\overset{-}{O}$) between the two rings, seems to react as if it contained two completely independent aromatic rings, both subjected only to the polar influences of the linking group and of such other substituents as they may contain. As in the closely corresponding benzoin series however (30), accurate quantitative research may reveal the existence of a very slight residual effect. Benzanilide, for example, should contain a still more effective damping linking group (*viz.*, $-NH-CO-$), yet, as has been mentioned, quite an appreciable amount of induced electrical polarity may be transmitted from ring to ring.

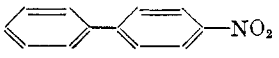
This characteristic decrease in intensity of both the polar influences owing to increasing distance of action, and to the intervention of intermediate groupings, is well illustrated by considering the series of compounds nitrobenzene (XXII), ω-nitrostyrene (XXIII) and nitrodiphenyl (XXIV), with which may also be exemplified the stages in the transition, in properties as well as in structure, from a simple aromatic compound to a linked aromatic ring compound.



(XXII)



(XXIII)



(XXIV)

Nitrobenzene is a kationoid system ($-I-T$), predominantly deactivating and *meta* substituting, whereas nitrodiphenyl—a benzenoid system—is much more reactive and is completely *ortho-para* substituting ($+T$). Even in the intermediate compound (XXIII) the presence of the linking $-CH=CH-$ group serves to reduce the tautomeric ($-T$) effect of the nitro group to a second order influence, far weaker than that of the nearer activating ($+T$) double bond (10).

In conclusion it may be stated that the study of linked ring systems shows most clearly the inherent properties and the distinctions between the general electron drift and the alternating tautomeric electron pulse effects, both of which can occur in aromatic compounds. The first influence (I), constant in action and electrostatic in character, can be transmitted over relatively great distances. It can act possibly through free space, and certainly through any intervening grouping. The second influence (*T*), of electrodynamic character, is temporarily very powerful indeed, but is essentially sporadic and variable in action. It can be transmitted only within readily mobile, completely conjugated, tautomeric systems. Even in these systems too, slight intermediate effects, originating in intervening atoms, may easily divert the path of the activating electromeric energy transmission or may modify its resultant intensity at any particular point within a molecule.

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