

266. *Significance of Tautomerism and of the Reactions of Aromatic Compounds in the Electronic Theory of Organic Reactions.*

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ABSTRACT.

The internal polar properties of atoms and groups may be classified either according to time-dependence or according to mechanism. The characteristics distinguished in the former classification differ in their physical dimensions (just as μ and a in $m = \mu + aF$). The effects categorised in the latter method of classification differ in the source of their energy. The two classifications are not quite co-extensive and their inter-relationship is considered. Therefore in addition to the inductive effect an inductomeric effect is recognised, the two being distinguished by their differing time-dependence. The tautomeric effect is split up into the mesomeric and electromeric effects on the same basis. Anomalous examples of orientation, reaction velocity, and chemical equilibrium are considered from the point of view indicated. The energy of the mesomeric effect is regarded as arising from a form of wave mechanical degeneracy (*Chem. and Ind.*, 1933, **52**, 434).

THE simplest molecular model which can serve as the basis for an electrical conception of reactions is that which visualises a distribution of atomic nuclei and electrons as point charges subject to elastic forces. In the development of the theory, the wave-mechanical ideas of a continuous statistical distribution of electron density, of quantised states, and of degeneracy, are introduced, but this does not affect the circumstance that the specification of the model requires two kinds of electrical quantities concerned respectively

with the positions and mobilities of the charges (van Vleck, "Electric and Magnetic Susceptibilities," 1932). The principal magnitudes describing gross intrinsic polarisations and polarisabilities of molecules, the dipole moment, μ , and the deformation coefficient, α , differ in dimensions by an amount corresponding to the dimensions of an electric force, and thus the total moment developed in the presence of a force is the sum of two terms, $\mu + \alpha F$, for a given direction. Recent work on molecular dipole moments has confirmed Thomson's suggestion (*Phil. Mag.*, 1923, **46**, 513) that these may roughly be calculated as the vector sum of group contributions. Such a calculation neglects intramolecular interaction, which is an essential matter in the theory of reactions; but it is often convenient to ascribe to groups an intrinsic moment, and treat the modifications caused by interaction as a superimposed effect. Similarly, the approximately additive character of refractivities shows that polarisability may also be regarded as a group characteristic, subject to modification by interaction. Thus groups also may be considered to possess a duplex electrical specification, provided the appropriate magnitudes are not treated strictly as constants. Reagents are regarded as acting by virtue of a constitutional affinity either for electrons or for nuclei* (Fry, "Electronic Conception of Valence," 1921; Stieglitz, *J. Amer. Chem. Soc.*, 1922, **44**, 1293; Lapworth, *Nature*, 1925, **115**, 625), and the organic molecule, in the activation necessary for reaction, is therefore required to develop at the seat of attack either a high or a low electron density as the case may be. Evidently the extent to which a given group can contribute to an activation is a duplex quantity, in which suitable measures of the polarisation, and the polarisability, of the group, and of the electrical demands of the reaction, play parts functionally analogous to those of μ , α , and F respectively in the above binomial. On several recent occasions, discussions have arisen because two reactions, each considered to test "polarity," do not place groups in an identical sequence; but it is evident that polarisation and polarisability are independent polar properties, and that the relative importance of the two contributory effects, dependent respectively on these group characteristics, must vary with the nature of the reaction.

Independently of such physical foundations, the electronic theory of valency limits the presumable forms of electron displacement by the principle requiring the preservation of stable electron groups. Displacements (\rightarrow in, e.g., $\text{Cl} \rightarrow \text{CH}_2 \rightarrow \text{CO}_2\text{H}$) throughout which the electrons concerned remain bound by their original atomic nuclei were postulated by Lewis ("Valence," 1923, p. 139); the mechanism was considered to illustrate a state of polarisation, and in subsequent organic chemical applications the designation *inductive* effect (Ingold, *Ann. Reports*, 1926, **23**, 140) has been employed as a convenient distinctive

term. Displacements (\curvearrowright in, e.g., $\text{R}_2\text{N} \curvearrowright \text{C}=\text{C} \curvearrowright \text{C}=\text{O}$) in which there is a substitution of one duplet for another in the same atomic octet were first assumed by Lowry (*J.*, 1923, **123**, 822, 1866; *Nature*, 1925, **114**, 376); the process was regarded as exemplifying an activation or polarisability effect, and this understanding is contained in the distinguishing term *electromeric*,[†] as introduced by Ingold and Ingold (*J.*, 1926, 1313) in relation to the mechanism.[‡] The synthesis of the two processes must be credited to Lucas and his collaborators (*J. Amer. Chem. Soc.*, 1924, **46**, 2475; 1925, **47**, 1459, 1462), who showed

* As Brönsted (*Rec. trav. chim.*, 1923, **42**, 718) and Lowry (*J. Soc. Chem. Ind.*, 1923, **42**, 43) have observed in reference to the special case of affinity for a proton (basicity), the state of electrification of a reagent is trivial in relation to so fundamentally constitutive a classification as that indicated in the text. For this reason the terms *electrophilic* (electron-seeking) and *nucleophilic* (nucleus-seeking) are suggested in place of the adjectives anionoid and cationoid introduced by Lapworth. Ammonia behaves as it does, not because it is like an anion, but because it is a base (more generally it is nucleophilic), and analogous reactivity is suppressed in the chloride ion, not, of course, because this is not a typical anion, but because it is not a base. Many cations are nucleus-seeking, e.g., the ferrous ion, and many anions electron-seeking, e.g., the permanganate ion.

† The term *electromerism* (= electron-tautomerism), which was introduced by Fry (*loc. cit.*), clearly contains the idea of mobility.

‡ A fuller outline should refer to the analogues of these mechanisms in pre-electronic theories of reaction, especially the theories of Flürsheim and Lapworth.

how the inductive effect may be supposed to direct and facilitate the electromeric (as, e.g., in $\text{CH}_3 \rightarrow \text{CH} \overset{\curvearrowright}{\text{C}} \text{H}_2$). The generalisation of these ideas, and the proof that, suitably developed, they yield a satisfactory interpretation of the numerous results concerning so extensive a group of reactions as those of aromatic substitution, were given by Robinson (J., 1926, 401) and Ingold (*ibid.*, p. 1310) and their collaborators, and elaborated further with reference to aromatic substitution by the subsequent investigations of both authors.*

In the further development of the theory, outlined later, the two mechanisms are not regarded as being *sharply* differentiated, the one as a permanent polarisation, and the other as a polarisability effect occurring in reaction, but it is recognised that the difference in time-dependence between the two processes lies in this direction. Slightly modifying an earlier suggestion, the terms *general inductive* (symbol I) and *tautomeric* (symbol T) may be used to distinguish the two mechanisms (denoted \rightarrow and \curvearrowright respectively), without reference to whether they represent a permanent molecular state or an activation phenomenon. Much evidence in favour of the view that the tautomeric effect is more time-variable than the general inductive effect may be adduced from the special refractivity contributions of simple and conjugated unsaturated systems,† and, in the field of organic reactions, a single example may be given to illustrate the consequences of this conception.

In aromatic substitution by electrophilic reagents, the normal correlation of *op*-orientation with nuclear activation and of *m*-orientation with deactivation is subject to certain exceptions, in which *op*-orientation and deactivation occur together, although the conjunction of *m*-orientation with nuclear activation is unknown. The orienting groups concerned in the known kind of anomaly all possess structures such that they exhibit opposing polar influences, and indeed they belong to the category of substituents which exert the effect symbolised $-I + T \ddagger$ (e.g., Cl in $\text{Cl} \overset{\curvearrowright}{\leftarrow} \text{Ar}$), although they constitute only a small section of that category (Ingold and Shaw, J., 1927, 2198). The interpretation offered concerning these facts starts from the difference in time-dependence already mentioned. Evidently a polarisation effect permanently conferred on the *op*-positions will be permanently relayed to the *m*-positions, whilst a corresponding polarisability effect will be absorbed by the exciting reagent, and therefore will not be relayed. It follows that the greater *op*-time-variability of the tautomeric than of the general inductive effect must be reflected in a greater *op*-selectivity of the former effect in its distribution over the aromatic nucleus. It is this difference of selectivity which makes provision for a class of orienting substituents showing the anomaly of *op*-orientation in conjunction with depressed nuclear reactivity. The anomaly will arise when, after the general inductive deactivation ($-I$ effect) of the whole nucleus, *m*-positions included, the tautomeric restoration of activity ($+T$ effect) selectively to the *op*-positions is strong enough to raise their reactivity above that of the still deactivated *m*-positions, but yet is not sufficiently strong to bring *op*-reactivity up to the standard of unsubstituted benzene. The matter is diagrammatically illustrated in Fig. 1. Groups of the $(-I + T)$ category are arranged horizontally in order of a diminishing $-I$ - and increasing $+T$ -component, whilst reactivity is measured vertically by a logarithmic function of the velocity of sub-

* The second paper was communicated before the first appeared. For a summary of further investigations by the writer and his co-workers in the field of aromatic substitution, see *Rec. trav. chim.*, 1929, 48, 797.

† Such contributions are sometimes included in so-called atomic constants, as may be illustrated by a comparison of the "constant" $[R_L]_D$ for nitrogen in NH_2 -Alkyl (2.45), NH_2 -Aryl (3.21), and NH_2 -C:C:C:O (4.88).

‡ Electron probability (density) being the physical variable concerned in a polar effect, it has been usual to write arrow signs in the direction of its positive increase, and to distinguish a positive increase as a $+$ effect, so that a $+$ effect is one which is activating towards electrophilic reagents. The suggestion (Baldwin and Robinson, J., 1932, 1445) of interchanging the customary prefix signs should be followed only in conjunction with a corresponding reversal of the arrows.

stitution at each nuclear position in terms of the velocity of substitution at a single position in benzene. If the general inductive effect operated alone, the points representing the activity of the various nuclear positions should yield curves such as a' and b' , which, if extended, should meet on or near the horizontal axis. The superposition of the tautomeric effect, and its great *op*-selectivity, are expressed by the large angular displacement of curve a' to position a , and the small, or zero, displacement of curve b' to position b . Curve a must now cut curve b before it cuts the axis, and thus the diagram becomes divided into three regions by the points of intersection, x and y . To the left of x is a normal region: curve b is above curve a (*m*-orientation) but below the axis (deactivation). The region to the right of y is also normal, since curve a is above curve b (*op*-orientation) and the uppermost curve is above the axis (activation). The abnormal region is comprised between x and y , and the anomaly there represented is of the type observed.

FIG. 1.

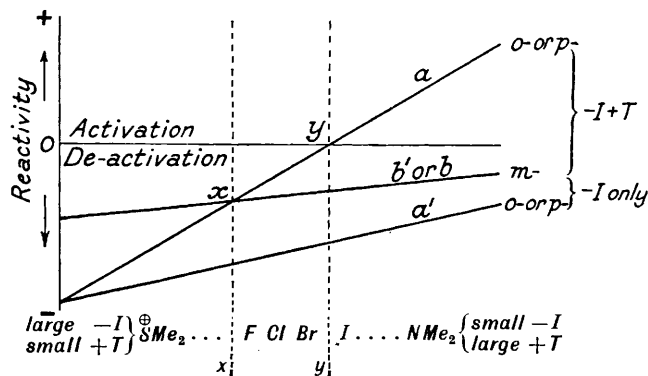
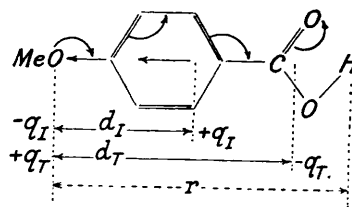


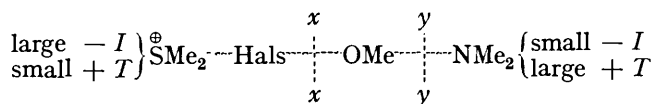
FIG. 2.



As already indicated, the recognition of the general inductive mechanism as a state of polarisation (inductive effect), and of the tautomeric mode of electron displacement as a polarisability (electromeric effect), is contained in the earlier development of the theory. The conception of a permanent polarisation associated with the mechanism of the tautomeric effect was first advanced by E. H. Ingold and the writer (J., 1926, 1312, *et seq.*); and a physical test for such a polarisation was proposed (Ingold, *Ann. Reports*, 1926, **23**, 149), which depended on finding a group ($\cdot\text{NMe}_2$ was suggested) such that, when it is linked to an unsaturated system, *e.g.*, phenyl, the polarisation effect of the kind sought opposes and is strong enough to outweigh the inductive effect; it then had to be shown by dipole moment measurements that the direction of the electric moment associated with the aliphatic union of the group ($\text{Alphyl}\overset{\oplus\ominus}{\rightarrow}\text{NR}_2$) is reversed in the corresponding aromatic combination ($\text{Aryl}\overset{\oplus\ominus}{\rightarrow}\text{NR}_2$). The first test of this kind was completed (for the group $\cdot\text{NH}_2$) by Höjendahl ("Studies of Dipole Moment," 1928) with definitely positive results, subsequently confirmed by other workers. Extensive further confirmation emerges from a generalised form of the same test conceived and applied by Sutton, who has shown (*Proc. Roy. Soc.*, 1931, *A*, **133**, 140) that, independently of the relative directions and intensities of component polarisations, the vector difference between the dipole moments associated with the types $\text{Alphyl}\cdot\text{R}$ and $\text{Aryl}\cdot\text{R}$ is in the direction of the tautomeric effect in the latter combination for a wide range of substituents, R. As Sutton's conclusions have been criticised on the grounds of his use of *tert.*-butyl and phenyl as arbitrary aliphatic and aromatic types, the view may be expressed that this necessarily arbitrary element in the theoretical treatment cannot affect the comparison of the groups, R, nor therefore the main significance ascribed to the results. The permanent polarisation associated with the tautomeric effect was originally distinguished by the name "electronic strain," but this term has not proved convenient and, on account of con-

siderations indicated later, the designation *mesomeric* effect is now substituted. A single example of the chemical significance of the effect may be given.

The normal relation between the direction of a group dipole and the effect of that group on the strengths of acids and bases is subject to a small number of exceptions in the aromatic series. The anomalies considered relate to substituents which permanently attract electrons, as is shown by the direction of their dipole contributions, but nevertheless depress the association of a suitably located carboxyl group. These substituents all belong to the class which exerts the effect symbolised $-I + T$, although they constitute only a small section of that category. Thus the methoxyl group, despite its electron-attracting dipole, decreases the strength of benzoic acid when introduced into the *p*-position. Since the effect illustrated has reference to an equilibrium, it must depend on the statistical condition of the system, and this includes factors relating to polarisation, polarisability, and entropy. It is highly improbable that the entropy effect can be responsible for more than a small proportion of the difference in free energy of dissociation between benzoic and *p*-anisic acids; and the polarisability effect works in the wrong direction, since the additional polarisability due to the methoxyl group in *p*-anisic acid must evidently increase the energy of dissociation. One is therefore thrown back on the polarisation effect of the methoxyl group, despite the difficulty concerning its direction, and the interpretation offered is that the opposing inductive and mesomeric components differ in their distribution, and, in particular, in their selectivity concerning the *p*-carboxyl group. Evidently the inductive effect will influence mainly the electrons of the aromatic nucleus, whilst the mesomeric effect will pass through the nucleus to the other extremity of the conjugated system, *viz.*, the carbonyl oxygen atom. A rough representation of the situation may be obtained by replacing the component effects by dipoles of different pole-strength, q , and pole-separation, d , as indicated in Fig. 2. The total polarisation due to the methoxyl group will be the sum of two terms, $-q_I d_I$ and $+q_T d_T$, and will correspond to electron attraction if the former term predominates, *i.e.*, if the excess of q_I over q_T is sufficiently large. On the other hand, the effect of the methoxyl group on the free energy of dissociation will contain terms proportional to $-q_T/(r-d_T)$ and $+q_I/(r-d_I)$, together with smaller terms in $1/r$ and polarisability and entropy corrections; it is clear that the first term might dominate the expression provided that the excess of q_I over q_T is not *too* large, and in that event the whole effect would be to weaken the acid notwithstanding the direction of the dipole. Generally, the anomaly illustrated will arise when the mesomeric polarisation, although weaker than the inductive, is not too weak to allow its greater selectivity to bring about a dominating influence over the dissociating group; and thus a series of substituents of the $(-I + T)$ -category, arranged as previously illustrated, will contain two critical points, one, y , where the dipole contribution changes direction, and the other, x , where the effect on the dissociating group changes sign, the central region thus marked off being the region of anomaly:



It cannot be doubted that a counterpart of two coexisting polarisations obtains also for polarisability effects, and that an inductive polarisability or *inductomeric* effect completes the scheme annexed: *

	General inductive (\rightarrow)	Tautomeric (\curvearrowright)
Polarisation	Inductive	Mesomeric (<i>M</i>)
Polarisability	Inductomeric	Electromeric (<i>E</i>)

The refractometric evidence of this need not be elaborated, but an example may be given in the field of reactions by reference to the problem of the polarity of alkyl.

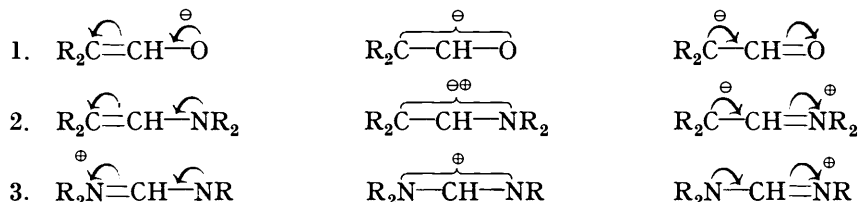
* The general inductive effect is regarded as being propagated partly outside the molecule (compare Lewis, *op. cit.*). This is the *direct* effect, introduced in relation to specific phenomena of reactivity and orientation by Ingold and Vass (J., 1928, 417), and extended by Bennett and Mosses (J., 1930, 2364).

groups are regarded as exerting a +I effect (e.g., $\text{CH}_3 \rightarrow$) relatively, as always, to hydrogen, notwithstanding that, according to the most acceptable definition of group dipole moments which also are relative to hydrogen [for a group \bar{X} , $\mu(\bar{X}) = \mu(\text{RX}) - \mu(\text{RH})$, where R is alkyl], the moment of the methyl group, and therefore of all alkyl groups, is zero. Evidently alkyl polarity is often induced by the groups the reactions of which are employed to demonstrate it (e.g., Cl or CO_2H). This may be proved by comparisons of dipole moments, e.g., (10^{-18} e.s.u.)



and a simple chemical example is provided by the strengths of formic, acetic, and propionic acids. On the other hand, a general inductive effect of the same kind persists *even in hydrocarbons* when the practical issue is reactivity towards an electrophilic reagent, as is illustrated by the orientation rules (Markownikoff) for the nitration of paraffins. Clearly, the polarisability of carbon is the important factor here, and thus, despite a zero moment, a condition such as $\begin{array}{c} \text{CH}_3 \searrow \\ \text{CH} \leftarrow \text{CH}_3 \\ \nearrow \\ \text{CH}_3 \end{array}$ may obtain during reaction. The possibility of an inductomeric (−I) effect of alkyl groups in the presence of nucleophilic reagents may be foreseen.

The energy necessary for a polarisability effect is assumed to be derived from without the molecule, but that associated with the polarisation must be contained within, and the existence of two modes of polarisation, in particular the occasional coexistence of opposing polarisations originating in the same atom or group, raises the question of the nature of the intra-atomic forces responsible for conditions so obviously incapable of interpretation on any purely electrostatic basis. The driving power of the inductive effect is evidently octet stability (including the influence thereon of nuclear charge and of inner electrons), and thus may be regarded as essentially quantum mechanical, if the success of the quantum theory in the interpretation of the duplet be taken as an earnest of its ability eventually to deal with the octet. The driving force behind the mesomeric effect cannot be the same (for the two effects may clash), and its nature therefore requires elucidation. This question may be approached by considering together the structures of an anion, a neutral molecule, and a cation, each constitutionally capable of the tautomeric effect. Each entity must have at least two normal modes of representation, as illustrated in the first and third of the columns of formulæ in the subjoined scheme; and the circumstance that some of the systems are charged as a whole whilst others are neutral as a whole, and that transitions may involve a displacement, a neutralisation, or even a separation, of local atomic charges, is trivial in comparison with the essential similarity of the three relationships exhibited. From the present point of view, the important



feature of the analogy is that all three systems show in greater or less degree the qualitative features of a wave-mechanical degeneracy. First, each pair of formulæ represents the same entity in different electronic states (hereafter called the unperturbed states); secondly, in one of the cases these states have the same energy, and in the others they may be assumed to have sufficiently nearly the same energy to preserve the essential features of the analogy; thirdly, it may be considered to be the principal significance

of the phenomenon of tautomerism that these states are coupled with respect to energy (compare Ingold, Shoppee, and Thorpe, J., 1926, 1481, and Cooper, Ingold, and Ingold, *ibid.*, 1868) in the sense of the perturbation theory. Mutual perturbations will therefore supervene, with the production of states which, by analogy with calculable examples of degeneracy, are expected to have lower energy than the unperturbed states, and therefore to correspond to the most stable condition of the system. Where there is an exact equivalence of unperturbed energies, the degenerate state must be symmetrically related to the unperturbed states, whilst in other cases the relationships, although not identical, must be similar (hence, the term *mesomeric* = between the parts); accordingly the degenerate or mesomeric states may be represented as shown in the centre column of the above scheme of formulæ, in which the symbol \frown denotes the distributed proper functions of the omitted electrons. Thus the independent source of energy without which the existence of the mesomeric effect would be impossible is identified as the energy of degeneracy.

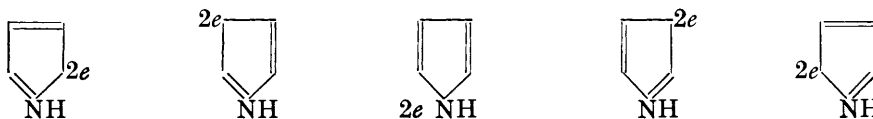
Empirical justification in favour of such a view is available within each of the three fields illustrated above. Example (1) represents prototropy, in the domain of which numerous pairs of hydrogen isomerides (keto- and enol, nitro- and *ac*inidro-, etc.) are known, but no single pair of corresponding alkali salts. The customary view that the single anion has a structure corresponding to that of the enol or *aci*-isomeride does not accommodate the optical activity of the nitro-anion (Kuhn and others, *Ber.*, 1927, 60, 1927, *et seq.*)* and the present suggestion is that the ion in all such cases has the mesomeric formulation. According to this view, observations proving the retention of optical activity during the bromination of a ketone (Leuchs and Wutke, *Ber.*, 1913, 46, 2435) would be interpreted on the grounds that in the halogenation of ketones the first step is, not enolisation as is usually stated, but ionisation, and that the mesomeric keto-enol anion may be capable of at least a transient optical activity. The same general indication emerges in the domain represented by example (3), although here the field of observations (Pyman, Mills) is less extensive; whilst the distinctive evidential contribution corresponding to case (2) is that afforded by measurements of dipole moments (Sutton), an experimental method which at present is unfortunately confined in application to neutral molecules. The whole trend of such general evidence as this receives corroboration from the detailed study of certain simple cases. Thus the carbonate ion has for some time been known to possess trigonal symmetry in the crystal, and the interpretation of infra-red and Raman spectroscopic data has led to the further conclusions that the linkings of the three oxygen atoms with carbon are associated with identical force constants and identical dipoles (Schaefer, *Trans. Faraday Soc.*, 1929, 24, 841). Again, according to the ordinary conception of the nitro-group, $-\overset{\ominus}{\text{N}}\begin{matrix} \text{O}^{\ominus} \\ \diagup \\ \text{O} \end{matrix}$, *p*-dinitrobenzene and 4:4'-dinitrodiphenyl should each have a large dipole moment (oriented perpendicularly to the line of the nitroxyl groups) just as have quinol ethers; actually, the dipole moments of these dinitro-compounds are both indistinguishable from zero (Williams, *Physikal. Z.*, 1928, 29, 174, 683), as the mesomeric structure, $-\overset{\oplus}{\text{N}}\begin{matrix} \text{O} \\ \diagup \\ \text{O} \end{matrix}\}^{\ominus}$, requires. The most recent example is that of the sulphur dioxide molecule, the two oxygen atoms of which have been concluded from spectroscopic evidence to be in all respects equivalent (Bailey and Cassie, *Proc. Roy. Soc.*, 1933, A, 140, 605).

In general, the fall in energy arising from a degeneracy of given order will be increased when the order of the degeneracy is raised by the participation of further unperturbed

* Kuhn's formula, $\text{RR}'\overset{\ominus}{\text{C}}-\overset{\oplus}{\text{N}}\begin{matrix} \text{O}^{\ominus} \\ \diagup \\ \text{O} \end{matrix}$, for the nitro-anion is derived by ionisation of the normal nitro-modification without distribution of the anionic charge thus produced, and should not be confused with the structure now advocated, $\text{RR}'\overset{\oplus}{\text{C}}-\overset{\ominus}{\text{N}}\begin{matrix} \text{O} \\ \diagup \\ \text{O} \end{matrix}\}^{\ominus}$, or more probably, $\text{RR}'\overset{\oplus}{\text{C}}-\overset{\oplus}{\text{N}}\begin{matrix} \text{O} \\ \diagup \\ \text{O} \end{matrix}\}^{\ominus}$, which alone involves the idea of distributed proper functions.

states, and an excellent example of the extent to which this effect may proceed can be seen in the stability of free radicals such as triphenylmethyl, where, owing to the large number of possible positions for the "free valency," the energy of degeneracy becomes comparable with the energy of the homopolar linking. This case has been treated in detail by Burton and the writer (*Proc. Leeds Phil. Soc.*, 1929, 1, 421), who described the theory now expressed in terms of distributed proper functions as a theory of "complex sharing," *i.e.*, of the *simultaneous* sharing of the same electrons by many atomic nuclei.* The same authors traced the source of energy of what is now called the mesomeric effect to the principles of electron identity and exclusion, the *modus operandi* of which is now attributed to degeneracy. Concerning free radicals in particular, it was shown also that the conditions appropriate to the stabilisation by degeneracy of the corresponding cation and of the anion should be simultaneously present in order to provide most effectively for the stabilisation of the radical.†

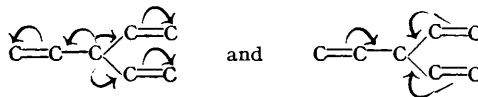
The interpretation of aromatic stability is an obvious application of the conception of tautomeric degeneracy, and, regarding the matter in this way, one perceives the inadequacy of envisaging the stability of five- and six-membered ring systems on an identical basis, as in the hypothesis of the aromatic sextet. In the six-membered rings (benzene, pyridine, etc.) the principal unperturbed states participating in the degeneracy will correspond to the various Kekulé (and Dewar) forms,‡ whereas the degeneracy in the five-membered systems (pyrrole, *cyclopentadienide* ion, etc.) will depend primarily on the multiplicity of possible positions for an unshared pair of electrons as is illustrated below for pyrrole :



The instability of the heterocyclic ring in ψ -isoindole, considered in contrast to the obviously aromatic nature of the corresponding ring in indole, is of considerable significance in this connexion, since, although both rings contain the necessary six electrons, that of ψ -isoindole lacks the equally essential multiplicity of unperturbed modifications (Goss and Ingold, J., 1928, 1268; Fenton and Ingold, J., 1928, 3295).§

The dipole moments observed in hydrocarbons such as toluene are possible manifestations of a general tendency towards the accumulation of electrons, *ceteris paribus*, in those regions of the molecule in which the largest amount of energy can be lost through degeneracy. Such an effect, if present, would naturally not be confined to hydrocarbons, but would be a factor in the polarisation of unsaturated compounds generally.

* The "electronic strain" theory (1926) is a theory involving *duplex* sharing, *i.e.*, partial sharing, or simultaneous sharing by *three* atomic nuclei; but "complex sharing" goes beyond this, inasmuch as it includes the idea of the spreading of the same electrons (*i.e.*, proper functions) *in several directions at once*, together with the complementary conception of *simultaneous electron confluence* consistent with the octet principle (cf. *loc. cit.*, p. 426, footnote): *e.g.*,



† [Added July 27th.] This theory is developed in a very recent paper by Pauling and Wheland, (*J. Chem. Phys.*, 1933, 1, 362), who have employed an extremely interesting method of wave-mechanical calculation.

‡ [Added July 27th.] Compare Pauling and Wheland (*loc. cit.*).

§ The "reaction formulæ" of previous papers on "The Structure of the Benzene Nucleus" (J., 1922, 121, 1133, 1143, *et seq.*), on "Intra-annular Tautomerism" (J., 1920, 117, 1362; 1922, 121, 128, *et seq.*), and on "Ring-chain Valency Tautomerism" (J., 1928, 365, *et seq.*) are evidently the unperturbed states of the present description.