626. *Polarisation in Conjugated Systems. Part V. The Polar Effect of the Halogens and Other Groups.*

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Theories of interaction between unsaturated hydrocarbon radicals and substituent groups are reviewed, with special reference to the mechanism of the inductive effect. The balance of evidence is in favour of the view that the latter is not altogether a short-range classical electrostatic phenomenon, but that it has a long-range non-classical component which must be explained in wave-mechanical terms.

The polarising effects of the halogens are considered in detail. Both theory and experiment support the view that they form π-bonds with conjugated systems, but this is not thought to be solely responsible for the apparent mesomeric moments (μ_m) in such systems; μ_m values for chlorobenzene and bromobenzene hardly alter when the conjugated system is extended (as in 4-chlorodiphenyl, etc.; see Part IV), which suggests that there is a balance between the mesomeric effect and the non-classical inductive effect beyond the first benzene ring, and probably that the net formal charge at the *para*-position is small. A discussion of how this arises is given.

μ_m is analysed into four terms, depending on : (i) the different electrostatic polarisabilities of the alkyl and aryl radicals used to obtain μ_m, (ii) the different σ-bond moments resulting from the different orbital hybridisation of carbon in these radicals, (iii) the non-classical inductive effect, and (iv) the acceptance or release of π-electrons by the substituent. Terms (iii) and (iv) determine the rate of increase of μ_m with extension of the conjugated system (see Part IV). Term (iv) can be separately evaluated when it is possible to twist the substituent by steric influences, and so prevent it from conjugating. The polarisations produced by certain common groups have been examined in these ways.

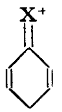
The theory of the interaction of substituent groups with unsaturated hydrocarbon radicals to which they are attached is familiar in its general outlines; and it has been assumed in the foregoing papers. We must now examine it more critically, however, particularly in its relation to the aryl halides. The language used to discuss the problem has been altered by the introduction of a more nearly deductive and semi-quantitative theory based on wave-mechanics; but the fundamental ideas remain much the same.

It is generally supposed that interaction may occur in two ways : (i) the electric field of the substituent group may polarise the radical (Robinson's and Ingold's *inductive effect*); (ii) the group may form a π-bond with the carbon atom to which it is attached, and this has repercussions on the π-bonds already in the radical (*mesomeric effect*, or formerly *electromeric* or *tautomeric effect*). In slightly different language, it participates in a molecular orbital with the carbon atoms of the radical. Both processes result in a drift of electrons to or from the substituent group, and they may reinforce or oppose each other.

Polarisation by the electric field has been visualised in two ways. On the one hand, it has been regarded purely as a classical electrostatic process, the moments induced in the various parts of the radical being severally equal to the product of the local field and the local polarisability which is assumed to be independent of field strength. If the bonds in the unsaturated radical have the same order and (hence) polarisability, *e.g.*, those in the phenyl radical, the induced moments would fall steadily with distance from the inducing dipole; otherwise, *e.g.*, in the butadienyl radical, there would be fluctuations about the falling mean. In either case, the inductive effect would die down rapidly. Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171) has shown by classical electrostatics that the moment induced at any point is proportional to the inverse cube of its distance from the polarising dipole, so that the inductive effect must be a relatively short-range one. An example of this is the rapid approach of moments to a limiting value as a homologous series of paraffin derivatives is ascended. This view of the inductive effect in conjugated systems has been taken recently by W. C. Price and Walsh (*Proc. Roy. Soc.*, 1947, *A*, **191**, 22).

On the other hand, induced polarisation has been regarded (*e.g.*, by Robinson, by Ingold, and by Wheland and Pauling) as a process involving not only the classical part just described, but also a non-classical part, in which the field of the substituent causes changes of π-bond order, as may be seen, *e.g.*, from the resonance representation of the situation (I). This could affect the whole of the conjugated system in the radical, just as the mesomeric effect does (II). Such "long-range" effects permit an explanation of the proportionality of the mesomeric moments to the length of the system, which was noted in Part IV; whereas the classical inductive effect certainly does not.

(I.)



(II.)

The two non-classical effects, unlike the classical one, cause changes of local charge only at alternate atoms, and, because they both act through the same medium (*viz.*, the π-bond system), they are not independent. Moreover, electron distributions in σ- and in π-bonds are not independent either, for a change of local charge in one will affect the other. This will be clearer when the wave-mechanical treatment is considered more fully.

The relationships between the effects are brought out in Table I.

TABLE I.

	Effect.	Medium.	Atoms affected.	Resonance representation.	Range.	Interdependence.	
Inductive	Classical	σ and π	All	—	Short		because changes of local charge in σ-bonds affect associated π-bonds, and *vice versa*.
	Non-classical	π	Alternate	(I)	Long	because both act through same medium	
	Mesomeric	π	Alternate	(II)	Long		

The Polar Effect of Halogens.—Both Robinson and Ingold suggested that the inductive and mesomeric effects in halogenobenzenes are opposed. The C–X dipole field *reduces* the negative charges on all the atoms in the ring, but especially (by the non-classical polarisation) on the *o*- and *p*-carbon atoms; the mesomeric effect *increases* the negative charge on these latter atoms. In the molecule unperturbed by the approach of a reagent, the differences of charge at the *o*-, *m*-, and *p*-positions are likely to be small; so it might be supposed that there would be little difference in reactivity at the several positions toward cationoid or electrophilic reagents. To overcome this difficulty it was postulated that the reagent could itself polarise the molecule and that the non-classical polarisations which involve conjugation with the substituent group are more important than those which do not; *i.e.*, there is greater polarisability at the *o*- and *p*-atoms than at the *m*-, so the former positions are predominantly attacked.

Some authors have questioned this explanation, because there is an apparent contradiction in the statements that (i) the halogen atom releases electrons to the hydrocarbon radical by the mesomeric process, and (ii) it pulls them away by the inductive process. Process (i) is particularly implausible when the halogen is fluorine. Baddeley and Bennett (*J.*, 1933, 261) suggested that the carbon–halogen bond dipole produces oppositely directed fields in its own vicinity and in that of the ring. C. C. Price (*Chem. Reviews*, 1941, **29**, 37; " Reactions at Carbon–Carbon Double Bonds," Interscience, 1946, Chap. I) and Leonard and Sutton (*J. Amer. Chem. Soc.*, 1948, **70**, 1564) have expressed similar views.

It might be hoped that the application of wave-mechanics to the problem would resolve such arguments by making a more fundamental discussion possible; but unfortunately a radically different treatment is not practicable. Certain points are, however, clarified. It has been demonstrated that a non-classical inductive process will augment the classical one in a conjugated system if the perturbing field is intense enough; a perturbation treatment (Coulson, Maccoll, and Sutton, to be published) has shown how the classical view breaks down by the development of " hyperpolarisability " in fields of the strength to be expected in the neighbourhood of dipoles and ions.

The origin of the π-electron drifts can be explained; and they can be treated semi-quantitatively by the molecular-orbital method. Molecular orbitals are constructed from two or more atomic π-orbitals, which each contribute to an extent depending on the electron affinity of the atom; so electrons in the molecular orbitals congregate mainly round atoms of high electron affinity, which may therefore be said to polarise the bond system as a whole. In a halogenobenzene, however, because the halogen contributes an already filled π-orbital to the π-bond system, it cannot thereby gain negative charge. On the contrary, it must release some, though the amount may be small because of the high electron affinity (see Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 56).

The electron affinity of an atom is affected by its environment: that of a carbon atom attached to a halogen, for example, is larger than normal because the C^+-X^- σ-bond dipole gives the carbon atom a positive charge. It also depends upon the π-electron charge on the atom (as well as *vice versa*) : if the halogen acquires a positive one, its electron affinity is clearly increased. Finally, the σ-bond dipoles are affected by the π-electron charges around them.

Several interacting, self-adjusting processes ought, therefore, to be considered, but in practice this cannot be done rigorously. What is usually done is to treat σ-bonds and π-bonds separately, and to suppose that the electron affinities are independent of π-electron distribution (see, however, Wheland and Mann, *J. Chem. Physics*, 1949, **17**, 264; Moffit, *Proc. Roy. Soc.*, 1949, *A*, **196**, 510). For the calculations, it is necessary to know the values of two sets of parameters which characterise respectively the atoms and the π-bonds between pairs of atoms, and which both depend upon the electron affinities. Neither set can be obtained *a priori*; both are commonly obtained by adjustment to give consistency in a series of related compounds or to give some desired answer such as that there is a residual negative charge at the *ortho*- and *para*-positions. It is common practice not only to consider the nature of the atom in assigning parameters of the first set, but to take account of its environment; the second set should similarly be adjusted for environment, but here this is less important, and it is not always done.

In the aryl halides the evaluation is particularly difficult because there is so delicate a balance between the mesomeric and non-classical inductive effects. It has proved necessary to add the assumption of the earlier theory, that polarisation by the reagent is a dominant factor; and this has been placed on a sound theoretical footing by Wheland and Pauling (*J. Amer. Chem. Soc.*, 1935, **57**, 2086), Wheland (*ibid.*, 1942, **64**, 900), and Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1947, *A*, **192**, 16).

As remarked above, it has been claimed that theory shows definitely the occurrence of π-bonding between the halogen and the radical (*idem, ibid.*, 1947, *A*, **191**, 56). Furthermore, two pieces of experimental evidence have a bearing. (i) Price and Walsh (*ibid.*, p. 22) have shown that the ultra-violet absorption spectrum of chlorobenzene is shifted to long wave-lengths relative to that of benzene, and hence that the first ionisation potential of the ring π-electrons in the former (8·77 v.) is lower than it is in the latter (9·24 v.). This indicates a drift of electrons into the ring. The same point is illustrated more strikingly by the decrease of the ionisation potential of benzene to 9·197 v. when fluorine is directly substituted on the ring, in contrast with the increase to 9·683 v. when the polar group CF_3 is substituted (Hammond, Price, Teegan, and Walsh, *Discuss. Faraday Soc.*, to be published). (ii) Goldstein and Bragg (*Physical*

Rev., 1949, **75**, 1453) have suggested that the microwave absorption spectrum of the analogous vinyl chloride can be plausibly interpreted only by postulating multiple bonding between the chlorine atom and the vinyl group.

The general conclusion is that the halogens do form π-bonds with conjugated carbon systems; and the apparent difficulty which is particularly prominent with fluorine, namely, that such bonding appears to be contrary to the electron-attracting character of these substituents, must be met by taking account of the possible gain of electrons through the σ-bond.

It does not appear that the difficulty is disposed of by the revision of the electron affinity of a gaseous fluorine atom by Evans, Warhurst, and Whittle (*J.*, 1950, 1524), who conclude that it is not more than that for chlorine and is very probably less : they remark, in effect, that, because the radius of covalently bound fluorine is small (whatever the cause of this may be), the field around it will be large.

Baddeley (*J.*, 1950, 663) has suggested that the overlap of the π-orbitals may be more favourable in fluorobenzene than in the other halogenobenzenes.

Evidence from Part IV.—In Part IV, values of an experimental quantity called the mesomeric moment were reported. This, being the vector difference between the moments of the aryl and alkyl compounds, should give the moment due to the non-classical polarisations, *i.e.*, to the mesomeric effect together with the non-classical part of the inductive effect. This is denoted as μ_m. It must, however, include also any error in allowing for the classical polarisation, and any non-compensating alterations in the C–X and C–H σ-bond moments due to change in the effective electronegativity or atomic radius of carbon when its hybridisation changes from sp^3 to sp^2. The importance of the latter effect has been suggested by Branch and Calvin (" Theory of Organic Chemistry," Prentice-Hall, 1941, p. 147) and by Walsh (*J.*, 1948, 398).

We saw in Part IV that when the apparent mesomeric moments, μ_m, of *p*-substituted aromatic systems are plotted against the lengths, *l*, of the systems, straight lines are obtained (Fig. 1, Part IV), the slopes of which ($d\,|\,\mu_m\,|\,/dl$) are characteristic of the polarising substituent (Table II, row 1).

TABLE II.

	NMe_2.	NH_2.	NO_2.	CN.	Ac.	Br.	Cl.
$d\,|\,\mu_m\,|\,/dl$	0·13	0·11	$0{\cdot}08_5$	$0{\cdot}05_6$	$0{\cdot}02_2$	$-0{\cdot}01_6$	$-0{\cdot}01_1$
$d\,|\,\mu_m\,|\,/dl$ (corr.)	0·13	0·11	$0{\cdot}07_0$	$0{\cdot}04_4$	$0{\cdot}02_2$	$-0{\cdot}00_3$	$+0{\cdot}01_1$

No distinction is made between electron-releasing and electron-accepting substituents, because the modulus, $|\,\mu_m\,|$, not μ_m, is taken.

It will be noticed that the halide series are exceptional, inasmuch as their mesomeric moments decrease in magnitude with extension of the system, whereas those of all the other groups increase. One possible explanation of this is the neglect of moments induced by the C–X dipole in the system beyond the first benzene ring (see above). Any error in allowing for the moment induced in the latter by the primary dipole is, however, at least common to all μ_m values in the series; so the only relevance of this induced moment is its secondary induction of a moment in the " tail," which is negligible. The moment *directly* induced in the latter by the C–X dipole is, however, just appreciable. Values for some compounds in the series have already been calculated by Le Fèvre and Le Fèvre (*J.*, 1936, 1116); their procedure has been followed, except that the polarising dipole has been taken as that of the appropriate group, and not that of the whole molecule. When these corrections for induction are applied, it is found that the changes in $d\,|\,\mu_m\,|\,/dl$ are quite small (see above table, row 2).

Two questions have therefore to be answered : (i) Why is $d\,|\,\mu_m\,|\,/dl \approx 0$ for the halogens? (ii) That being so, why is $\mu_m \neq 0$, *i.e.*, why is the moment of an aryl halide different from that of an alkyl halide?

The first question may be re-phrased : Why is there no long-range polarisation in the aryl halides? To this, the most probable answer is that the mesomeric effect and the non-classical inductive effect, which would be opposed in the aryl halides, nearly cancel beyond the first benzene ring. This does not necessarily mean that the net moment due to non-classical π-electron rearrangements in the fragment $X{\cdot}C_6H_4{\cdot}$ is zero, because the systems involved in the two effects are different (formulæ I and II); but it is likely to be small. It probably means that the net formal charge at the *p*-position is very small. That such a condition could actually arise from an accidental relation between the electron affinity parameters, δ, defined by Wheland and Pauling (*loc. cit.*), and that this relation is a possible one, may be seen from Fig. 1, based on two sets of parameters which they considered. It appears that μ_m could be small and its direction uncertain; likewise, that the charge on the *p*-position could be very small and its sign indeterminate. These calculations require extension to stilbene and diphenyl compounds. Also, since it is, of course, unlikely that $d\,|\mu_m|\,/dl$ would be so near zero for all the halogens, it would be of great interest to obtain values for the full series of fluoro- and iodo-compounds.

FIG. 1.

Electron distribution in a halogenobenzene (in units of $-e/100$; i.e., *positive charges are given positive signs).*

(*a*) $\delta_X = 4$; all other δ values $= 0$. $\mu_m = +0{\cdot}86\ (\downarrow)$.

(*b*) $\delta_X = 4$; $\delta_1 = 0{\cdot}4$. $\mu_m = -0{\cdot}22\ (\uparrow)$.

If this hypothesis be correct, we must conclude that the reason why $\mu_m \neq 0$ is that there may be some contribution from π-electron rearrangement (though less than is commonly supposed), some error in allowing for classical polarisation, and some effect due to change of hybridisation of the carbon atom, and possibly also of the halogen atom. It has been argued that sp^2-hybridised carbon has a higher electronegativity than has sp^3-hybridised carbon (Walsh, *loc. cit.*), which would make the C–X σ-bond dipole smaller in aryl than in alkyl compounds. Against this must be set the effect of the formal charges on the carbon and halogen atoms due to π-electron rearrangement, which are such as to increase the σ-bond moment.

The Polar Effects of Other Groups.—If the conjectures in the preceding section are correct, the " mesomeric moment " of any compound (as defined in Part IV) can be analysed into four terms, which depend on, respectively :

(i) the different classical electrostatic polarisabilities of the saturated and the aromatic radicals which are used to obtain μ_m;

(ii) the different C–X and C–H σ-bond moments in the saturated and the aromatic compounds;

(iii) the non-classical inductive effect; and

(iv) the mesomeric effect proper, *i.e.*, the acceptance or release of π-electrons by the substituent.

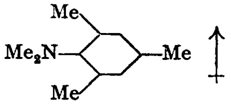
The quantity $d\,|\mu_m|\,/dl$ measures the effect of terms (i), (iii), and (iv) only; and when a correction is made for induction, as in Table II (row 2), the effect of (i) is eliminated also. It is therefore a truer measure of the π-bond polarising power of the substituent than is the mesomeric moment.

Term (iv) can be separately evaluated in compounds with a substituent which can be twisted at right angles to the plane of the aromatic system, by steric blocking. The moment of nitrodurene, for example (3·62; Kofod and Sutton, unpublished), unlike that of nitrobenzene (4·01), does not include any contribution from term (iv), because the nitro-group cannot conjugate with the ring. Since the sum of the induced dipoles in the methyl groups vanishes (Birtles and Hampson, *J.*, 1937, 10), the difference (0·39) between these two moments must represent term (iv) in nitrobenzene; *i.e.*, it represents the ability of a nitro-group to accept π-electrons from a phenyl radical. If the conjugation is not completely inhibited, this value would be a lower limit.

The same treatment can be applied to dimethylmesidine ($\mu = 1{\cdot}03$; Ingham and Hampson, *J.*, 1939, 981), for which spectroscopic data indicate that conjugation is entirely inhibited (Klevens and Platt, *J. Amer. Chem. Soc.*, 1949, **71**, 1714). A difficulty arises in that the sense of the total moment is not obvious, *i.e.*, whether the negative or the positive pole is directed away from the ring. However, the ambiguity can be resolved by using the moment of dimethyl-2 : 6-xylidine (0·94; Fischer, *Acta Chem. Scand.*, 1950, **4**, 1197). This sterically hindered compound differs from dimethylmesidine in having an extra moment of 0·35 (the moment of toluene or *m*-xylene) directed along the 1 : 4-diagonal with its negative end away from the NMe_2 group. The component of the moment of dimethylmesidine resolved at right angles to the 1 : 4 diagonal is found to be 0·79 (from the moment of tetramethyl-*p*-phenylenediamine); so the component along the diagonal must be $\sqrt{(1{\cdot}03^2 - 0{\cdot}79^2)} = \pm 0{\cdot}66$. From these, and the moment of toluene, we can calculate two alternative values for the moment of dimethyl-

2 : 6-xylidine, *viz.*, 1·28 and 0·85. The latter, from −0·66, agrees with the observed value of 0·94, showing that the moment along the 1 : 4 diagonal in dimethylmesidine has its negative pole towards the NMe_2 group (Fig. 2). Hence, by taking away the σ-bond moment (see Part IV), the mesomeric moment is −0·66 + 0·28 = −0·38, *i.e.*, also towards the NMe_2 group, and in the *opposite* direction to that in dimethylaniline (+1·66).

FIG. 2.



0·79 *component at right angles to* 1 : 4 *diagonal*

0·66	←—+	*total moment in dimethylmesidine* } *resolved along* 1 : 4 *diagonal*
0·28	+→	*σ-bond moment in dimethylmesidine* } *resolved along* 1 : 4 *diagonal*
0·38	←+	*mesomeric moment in dimethylmesidine*
1·66	+——→	*mesomeric moment in dimethylaniline*
2·04	+———→	*term* (*iv*) *in dimethylaniline*

This result might have been expected because, although in dimethylmesidine term (iv) of the mesomeric moment is eliminated, yet term (iii), which opposes it, remains. Evidently, term (iv) in dimethylaniline is 1·66 + 0·38 = 2·04.

If it can be assumed that the mesomeric moment of a hypothetical aniline molecule in which the amino-group does not conjugate with the ring is also 0·38, then term (iv) in aniline is only 1·40. This quantity cannot be obtained except by analogy, because the *N*-hydrogen atoms in mesidine are not big enough to suppress, by their interference with the *o*-methyl groups, the conjugation of the amino-group with the ring. Nevertheless, the conclusion that nitrogen parts more easily with π-electrons when it has two methyl groups attached than when it has two hydrogen atoms is almost certainly correct; and the moment of 4-diethylaminostilbene (2·69) compared with those of diethylaniline (1·65; Krasil'nikov, *J. Phys. Chem. U.S.S.R.*, 1944, **18**, 174: 1·81; Barclay, Le Fèvre, and Smythe, *Trans. Faraday Soc.*, 1951, **47**, 357), dimethylaminostilbene (2·41), and dimethyl aniline (1·61), suggests that with ethyl groups the effect is still greater. It should therefore be clear that in molecular-orbital treatments of conjugated molecules it is not legitimate, unless the treatments are to be unnecessarily rough, to consider electron affinity parameters as characteristic solely of the atoms concerned; they must depend quite markedly on whether the atoms bear hydrogen or alkyl groups, and allowance should be made for this (cf. Orgel, Cottrell, Dick, and Sutton, *Trans. Faraday Soc.*, 1951, **47**, 113).

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