234. *The Magnitudes and Signs of the Inductive and Mesomeric Effects of the Halogens.*

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From ground-state properties it has been deduced that the halogens are electron-attracting ($-I$) in the order F > I and electron-donating ($+M$) in the order F > I. Spectroscopic evidence gives the reverse order for the donating ($+M$) effect and the opposite sign ($+I$) for the inductive effect. It is shown that there are two reasons for this disagreement. First, from ground-state properties one measures the difference between any ($+M$) and ($-M$) effect whereas from spectroscopic evidence one measures the sum of these effects. Secondly, the spectroscopic data give a measure of the inductive effect on π-electrons only (I_π). The accepted ground-state order of the mesomeric effect is really a measure of the sum of the ($+I_\pi$) and the ($+M$) effect.

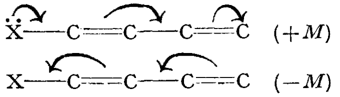
THE changes in electron density which occur in an organic molecule on substitution are usually described by reference to the inductive and mesomeric properties of the substituents.[1] These terms were originally defined by reference to the classical theory of valency or to its quantum-mechanical equivalent, the valence-bond theory. The inductive effect describes the tendency for a substituent to attract or repel electrons according to its electronegativity, without changing the arrangement of the electron pairs in the molecule. The mesomeric effect, which only occurs in unsaturated molecules, describes the tendency of the substituent to extend the conjugation path by rearranging the electron pairs in the unsaturated molecule. This involves either donation of an electron to the unsaturated molecule, or acceptance of an electron from the unsaturated molecule. These two effects are depicted by the following symbols:

Inductive effect

$X \rightarrow C \rightarrow C \rightarrow C$ ($+I$)

$X \leftarrow C \leftarrow C \leftarrow C$ ($-I$)

Mesomeric effect



From the physical and chemical properties of the ground states of halogenated molecules it has been concluded that the halogens have a $-I$ effect (electron-attracting) and a $+M$ effect (electron-donating), and in the halogen series these effects are greatest for fluorine and least for iodine:

$$\mathrm{F} > \mathrm{Cl} > \mathrm{Br} > \mathrm{I} \quad (-I) \qquad (1)$$

$$\mathrm{F} > \mathrm{Cl} > \mathrm{Br} > \mathrm{I} \quad (+M) \qquad (2)$$

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[1] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953.

On the other hand, from spectroscopic evidence,[2-5] mainly from the shift in the 2600 Å absorption band of benzene, it is deduced that the halogens are electron-repelling (+*I*), in the order

$$\mathrm{F} > \mathrm{Cl} > \mathrm{Br} > \mathrm{I} \quad (+I) \qquad (3)$$

and electron-donating in the order

$$\mathrm{I} > \mathrm{Br} > \mathrm{Cl} > \mathrm{F} \quad (+M) \qquad (4)$$

The disagreement on the order of the mesomeric effect has been known for a long time, but no explanation has been given. The disagreement on the sign of the inductive effect, which is the more important, has not been remarked. We shall show that the disagreement in the order of the mesomeric effect is tied closely to the disagreement in the sign of the inductive effect.

To analyse the spectroscopic data quantitatively by quantum mechanics it is necessary to be rather precise about the definitions of the substituent effects: they must be definitions which can be expressed in mathematical terms. The following are usually adopted. If a group X just changes the potential acting on the electrons of the hydrocarbon R, it is said to exert an inductive effect. Providing we know the form of this potential we need take no further notice of the electronic structure of X. If X has an orbital (whether this is occupied by electrons or not), which has the same symmetry as the orbitals containing the delocalized electrons of the hydrocarbon (π-orbitals), then these π-orbitals can be taken to extend the conjugated system. The extent to which the unsaturation electrons are delocalized over X and the hydrocarbon is a measure of its mesomeric effect. These definitions are in sympathy with the more qualitative definitions given earlier.

Mathematically, the magnitude of the inductive effect is given by the amount that the energy levels and wave functions of the hydrocarbon are changed by the potential field of the substituent. The magnitude of the mesomeric effect is given by the extent of the interaction between the states of the type RX and the ionic states R^+X^- and R^-X^+. The extent of this interaction depends primarily on the relative energies of the states involved. The halogens are predominantly electron-donors, and the order of mesomeric strengths (4) is in accordance with the decrease in energy of the states R^-X^+ as determined by the ionization potentials of the halogens, F > I. In order to explain the order (2) we have to suppose that there is a larger interaction between the ground state and the ionic states for fluorine than for iodine, even though the energies of the states R^-F^+ are much higher than those of the states R^-I^+.[6]

It has been shown that if the definitions given above are adopted the mesomeric effect changes the frequency of the benzene 2600 Å band by an amount which is merely additive for each group introduced:[7] for homo-substitution the shift is proportional to the number of substituents. The inductive effect, on the other hand, gives a frequency shift which is sensitive to the relative position of the substituents: *ortho-*, *meta-*, and *para-*substitution would cause the same mesomeric shift but different inductive shifts. By separating the observed frequency shift into a part which is additive in substituents and a part which is not, one can deduce the magnitudes of the inductive and the mesomeric effect.[7] From the benzene spectrum (or from the spectra of alternant hydrocarbons in general) one determines absolutely the magnitude, but not the sign, of the inductive effect.[2] However, if the sign can be assumed for one group [*e.g.*, the introduction of a nitrogen atom into the

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[2] Murrell and McEwen, *J. Chem. Phys.*, 1956, **25**, 1143.

[3] Forbes, *Canad. J. Chem.*, 1956, **34**, 1447.

[4] Forbes, *Canad. J. Chem.*, 1961, **39**, 2295.

[5] Petruska, *J. Chem. Phys.*, 1961, **34**, 1120.

[6] Tedder and Henne, *Ind. Chim. belge*, 1954, **19**, 695; Baddeley, *J.*, 1950, 663.

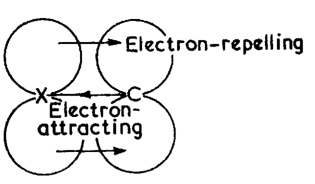
[7] Murrell, *Proc. Phys. Soc.*, 1955, **68**, *A*, 969.

ring attracts electrons ($-I$)], then all other groups can be measured relative to that one.[3, 5] This is analogous to the method of obtaining the signs of bond dipole moments. From such an analysis the halogens are definitely shown to be $+I$ substituents. Support for this sign can be obtained from substituent effects on the spectra of non-alternant hydrocarbons. Chlorine gives a bathochromic shift to the first band of azulene [8] when introduced into the 1-position, and this is in agreement with its being a $+I$ group. Conclusive evidence from this field would be the observation of a hypsochromic shift from 2-halogenated azulenes, but the spectra of these have not been measured.

From the benzene spectrum one deduces the magnitude of the mesomeric effect but not its sign. Moreover, donor and acceptor properties of the substituent combine to give a bathochromic shift to the benzene 2600 Å band. The mesomeric order (4) is, therefore, derived on the assumption that the accepting powers of the halogens can be neglected in comparison with their donating powers. This is probably correct for fluorine and chlorine, but is less certain for the heavier halogens.[9] From ground-state properties, however, one obtains evidence about the difference between the donating and the accepting strength of the substituent. Only if the substituent is either a pure donor or a pure acceptor will the ground state and the spectral mesomeric strengths be the same. To some extent, therefore, the difference between the mesomeric orders (2) and (4) lies in the neglect of the accepting power of the halogens.

The evidence for the ground-state orders (1) and (2) is based on the following type of analysis. The inductive effect is determined from the effect of the halogen on the properties of a saturated system; for example, the strength of the halogenated bicyclo[2,2,2]octane acids relative to the strengths of the unsubstituted acid.[10] The same inductive effect is then assumed to be present in an unsaturated system, and any factor which cannot be explained on the basis of that inductive effect is attributed to the mesomeric effect. For example, the *p*-halogenobenzoic acids are stronger than benzoic acid, as they should be from the influence of a $-I$ effect, but the increase is smaller for fluorine than for chlorine.[11] There must be a compensating effect (taken to be the mesomeric effect) which is greater for fluorine than for chlorine. In the same way, the halogens deactivate the benzene ring to electrophilic substitution, yet are *ortho/para*-directing, and again the $+M$ effect compensates for the $-I$ effect.

The assumption to be questioned in the analysis of the ground-state properties is that the inductive effect is the same for saturated and unsaturated systems. The spectroscopic evidence (which concerns only the electrons undergoing the electronic transition, namely, the π-electrons) shows that, even though the halogens attract σ-electrons, they repel π-electrons. The halogens are σ-electron-attracting by virtue of their greater electronegativity than carbon, which arises from their desire to complete an inert-gas structure. Certainly, at large distances from the C–X bond, the electrons, both σ and π, will be under the influence of the field of the C–X bond dipole, which will attract electrons towards the substituted carbon atom. However, the π-electrons which are close to the substituted atom, in particular those lying on the substituted atom will not be dominated by this dipole field, but by the repulsion of the halogen lone-pair electrons which have π-symmetry (cf. Figure).



Not only are the inductive effects on σ- and π-electrons of opposite signs, but also they give rise to different types of electron redistribution in the molecule. If in a saturated chain the potential at one end is lowered, there is a general drift of electrons down the chain towards this potential dip. The depletion of electrons from the atoms in the chain

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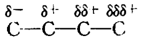
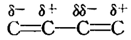
[8] Anderson, Nelson, and Tazuma, *J. Amer. Chem. Soc.*, 1953, **75**, 4980.
[9] Goodman and Frolen, *J. Chem. Phys.*, 1959, **30**, 1361.
[10] Roberts and Moreland, *J. Amer. Chem. Soc.*, 1953, **75**, 2161.
[11] Dippy, *Chem. Rev.*, 1939 **25**, 151.

falls off rapidly and smoothly as the distance from the dip increases. We can illustrate this as follows:



$$\overset{\delta-}{\mathrm{C}}-\overset{\delta+}{\mathrm{C}}-\overset{\delta\delta+}{\mathrm{C}}-\overset{\delta\delta\delta+}{\mathrm{C}}$$

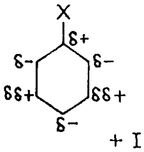
On the other hand, if we do the same thing for π-electrons the effect is propagated over a much longer range than with a saturated chain, but, more importantly, electrons are only withdrawn from every other atom in the chain, and there is in fact a small increase in electron density at the other atoms. This is illustrated as follows:[12]



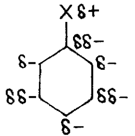
$$\overset{\delta-}{\mathrm{C}}=\overset{\delta+}{\mathrm{C}}-\overset{\delta\delta-}{\mathrm{C}}=\overset{\delta+}{\mathrm{C}}$$

The change in π-electron density at atom r brought about by a change in the potential of an electron at atom s is known as the atom–atom polarizability π_{rs}[12]; in benzene a $+I_\pi$ effect on π-electrons removes electrons from the position of substitution, builds up electron density at the *ortho*- and the *para*-position, and reduces the electron density slightly at the *meta*-positions. This is somewhat similar to the density changes produced by a $+M$ effect. Valence-bond theory predicts an increase in density at the *ortho*- and the *para*-position and no change at the *meta*-positions or position of substitution. Molecular-orbital theory would predict an increase in density at these last two positions also, but a smaller increase than in the *ortho*- and *para*-positions. We can summarize the $+I_\pi$ and $+M$ effects by the diagrams below.

If we are just looking at some property of the molecule which depends only on electron density, then an increase in electron density at the *ortho*- and the *para*-position may be due to a $+I_\pi$ or to a $+M$ effect, or to both. It is the failure to recognize the $+I_\pi$ effect of the halogens that has led to the difference between the order of mesomeric strengths (2) and (4). The order (2) is really a measure of the sum $(+I_\pi) + (+M)$, the total of *ortho*/*para*-directing effects.



+ I_π



+ M

If one is trying to separate the $+I_\pi$ and $+M$ effects just from the ground-state electron density, then the density in the *meta*-position will be more informative than that in the *ortho*- and *para*-positions. The $+I_\pi$ effect deactivates the *meta*-position, the $+M$ effect activates it.

More detailed calculations are needed to give an accurate picture of the electron densities induced in a hydrocarbon by a substituent, and until these are known a quantitative analysis of the ground-state properties in terms of mesomeric and inductive parameters will not be possible. However, the two facts which have been emphasized in this paper, namely, the electron-accepting property of halogens and their $+I$ effect on π-electrons, go a long way towards reconciling the ideas of the spectroscopist and the organic chemist.

THE UNIVERSITY, SHEFFIELD, 10. [*Received, July* 12*th*, 1962.]

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[12] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39.