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Induction, Resonance and Dipole Moment*

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Induction plays such an important role in the use of dipole moments for the examination of molecular structures that it has seemed worth while to obtain certain new moment values and to redetermine by measurements on vapors some moments previously determined in solution and used to draw conclusions as to inductive effects. It is desirable, at the same time, to reappraise the conclusions drawn from earlier data in the light of new information and to point out difficulties which remain. The question of bond moment values is intimately connected with the problem of induction and with that of resonance and will be discussed in these connections. The quantitative determination of resonance from dipole moment, the discussion of which is another object of this paper, is also dependent upon these questions of induction and bond moment. The effect of induction as discussed here is the displacement of charge in a molecule by the ordinary electrostatic forces exerted by other charges in the molecule, these other charges being treated here commonly as forming dipoles and producing additional dipoles by their inductive effects.

The increases in moment of the alkyl halides and some other alkyl compounds on going from the methyl to the ethyl compound and of the butyl halide moments on going from primary to secondary to tertiary were attributed to dipoles induced by the carbon–halogen dipole in the groups immediately attached to the primary carbon.[1] The methyl-to-ethyl moment increase was found, through vapor measurements, to increase by 0.07 × 10^{-18} for each change from fluorine to chlorine to bromine to iodine.[2] Groves and Sugden[3] proposed a qualitative explanation of this change in the increase in terms of the size of the halogen atom and an effect of the hydrocarbon chain upon the field of the primary dipole, but, of necessity, left the question in a vague state. They concluded from additional vapor measurements listed in Table I that there was a further small moment increase on going from ethyl to propyl, the increase again becoming greater on going from the chloride to the bromide to the iodide. They reported a still smaller increase on going from propyl to butyl, although it was large enough to be experimentally significant only in the case of the iodides. These results of Groves and Sugden are, on the whole, consistent with the fact[4] that, in the halogenated fatty acids, the presence of the halogen increases the ionization constant of the acid to a decreasing extent as the halogen is moved along the carbon chain away from the carboxyl group, although a slight increase is still apparent when the halogen is on the δ-carbon. It has been pointed out,[4] however, that the ionization constant should be more sensitive than the dipole moment to small displacements of charge.

The moments of homologous series measured by Groves and Sugden[3] or assembled by them from the literature are given in Table I together with values for the butyl chlorides and nitroparaffins measured by Dr. R. H. Wiswall in this Laboratory and designated by a W after each value. The values listed by Groves and Sugden are calculated from the difference between the total polarization and the sum of the molar refraction for the sodium D line plus 5% of this molar refraction to take care of the atomic polarization. The omission of this added empirical allowance for the effect of atomic polarization should make Wiswall's values 0.01 to 0.02 × 10^{-18} higher than the values of Groves and Sugden for the same compounds and 0.04 higher than those found by Smyth and McAlpine from the variation of polarization with temperature.[2]

Although the probable error given by Groves and Sugden for their results is only 0.01 × 10^{-18} and that in Wiswall's values is 0.02 × 10^{-18}, greater discrepancies are occasionally apparents which are, presumably, to be attributed to impurities or to errors in the measurements. When the considerable discrepancy between Wiswall's values for the nitropropanes and those of Groves and Sugden for the nitroparaffins was noted, nitromethane was measured as a check on the accuracy of the determinations. The exact

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(1) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc., New York, N. Y., 1931, pp. 75, 102.

(2) Smyth and McAlpine, *J. Chem. Phys.*, **2**, 499 (1934).

(3) Groves and Sugden, *J. Chem. Soc.*, 158 (1937).

(4) Ref. 1, p. 133.

TABLE I

DIPOLE MOMENTS ($\times 10^{18}$) IN THE VAPOR STATE OF HOMOLOGOUS SERIES

	Cl	Br	I	CN	NO_2		OH
CH_3	1.87	1.80	1.64	3.94	3.54	3.50W	1.69
C_2H_5	2.05	2.01	1.87	4.04	3.58		1.69
n-C_3H_7	2.10	2.13	2.01	4.05	3.57	3.72W	1.65
n-C_4H_9	2.11	2.15	2.08	4.09	3.55		1.65
n-C_5H_{11}	2.12						
i-C_3H_7	2.15	2.19				3.73W	1.63
n-C_4H_9	2.09W						
i-C_4H_9	2.04W						1.60
s-C_4H_9	2.12W	2.20					
t-C_4H_9	2.13W					3.71W	

agreement of the polarizations found for nitromethane with those found by Smyth and McAlpine[5] some years ago makes it appear highly probable that the increase in moment from nitromethane to nitropropane is about 0.22×10^{-18}. However, the fact that $(CH_3)_2CHNO_2$ and $(CH_3)_3CNO_2$ have moments indistinguishable from $CH_3CH_2CH_2NO_2$ confirms the conclusion to be drawn from Groves and Sugden's values for the straight chain compounds that the inductive effect of the dipoles of the nitro group is not detectable in the moments beyond the first two carbons of the chain. This is understandable since the carbon–nitrogen bond moment is small[6] and the large nitrogen–oxygen bond moments are separated by the nitrogen from the carbon chain. The small size of the inductive effect calculated approximately by Groves and Sugden conforms qualitatively to these facts, although the observed inductive effect is larger than the calculated. In the cyanides the large dipole lying between the carbon and nitrogen of the cyanide exerts a considerable inductive effect only as far as the β-carbon. The effect beyond this is of the magnitude of the experimental error. The carbon–halogen dipoles are about half as large as the cyanide and nitro group dipoles and should, therefore, exert about half as large an inductive effect upon the γ-carbons as the latter do upon the β-carbons. This is evidenced in the increase of moment from ethyl to n-propyl chloride, beyond which any further increase in moment is no larger than the experimental error. The greater and farther extended increase in the bromides and iodides was attributed by Groves and Sugden to the effect of the chain upon the field of the dipole and, in turn, its effect upon the halogen atom. The increase in moment from the n-propyl to the i-propyl chloride and bromide and from the normal to the secondary to the tertiary butyl chloride is caused, as previously indicated, by increase in the amount of polarizable matter within the effective range of the principal dipole. The increase is less than would be anticipated in view of the increase from the methyl to the ethyl compounds, but it must be remembered that, in the i-propyl and s-butyl compounds, the induced dipoles partially oppose one another, while, in t-butyl chloride, only the components of induced dipoles in the carbon–chlorine axis are effective in increasing the moment of the molecule as a whole.

Within the limitations imposed by experimental error and the uncertainties in the calculations resulting from the treatment of the charge distribution as a single dipole located at a point, whose exact location is not really known, it is evident that the effects of induction may be estimated fairly satisfactorily for these compounds. In the cases of the alcohols and ethers when two dipoles are close together at the oxygen atom, the calculation of inductive effects must be so uncertain as to render extremely doubtful the value 2.30 calculated by Groves and Sugden[7] for the C–O bond moment, a value completely out of line with that estimated previously and with those of other single covalent bond moments.[8] The previously advanced explanation of the absence of an increase in the moments of the aliphatic alcohols with increase in the carbon chain as being due to the angle of the resultant of the C–O and H–O dipoles with the direction of the chain[9] may now be amplified, the small C–O bond moment value 0.9 previously calculated[6] being used. The small C–O moment should induce small moments in the carbon chain, tending to increase the molecular moment with increasing chain length as in the alkyl halides, though to a smaller extent be-

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[5] Smyth and McAlpine, THIS JOURNAL, **56**, 1697 (1934).

[6] Smyth, *ibid.*, **60**, 183 (1938).

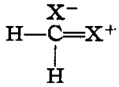
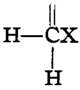
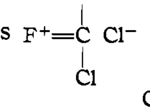
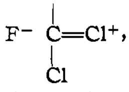
[7] Groves and Sugden, *J. Chem. Soc.*, 1992 (1937).

[8] Smyth, *J. Phys. Chem.*, **41**, 209 (1937).

[9] Ref. 1, p. 88.

cause of the smaller primary moment. If the larger H–O moment 1.5 were located in a *trans*-position relative to that of the methyl group in ethyl alcohol, it would exert little effect upon this group, but, if it were in a *cis*-position, the not inconsiderable moment induced by it should oppose and tend to reduce that of the molecule as a whole. The average effect of the H–O moment should come close to compensating the effect of the C–O in increasing the moment of ethyl over that of methyl alcohol, leaving the two nearly if not quite the same, as observed. Branching or lengthening of the chain can bring additional polarizable matter within the range of the H–O dipole in its *cis*-position, where it should decrease the total moment slightly as apparent in Table I. Although there is a small but considerable increase in moment on going from acetaldehyde to acetone, the absence of any considerable increase on lengthening the carbon chain in acetone is natural in view of the smallness of the increase in the cases of the cyanide and nitro compounds which have considerably larger moments.

The moment of methyl chloroform should be higher than that of chloroform because of the inductive action of each of the three C–Cl dipoles upon the methyl group. The moment thus produced by each dipole may be estimated to be a little smaller than that arising from the action of the C–Cl dipole in ethyl chloride upon the methyl group, which causes an increase in moment of 0.18 from methyl to ethyl chloride in Table I. Three times this increase or 0.54 is, therefore, the maximum increase to be expected in methyl chloroform as compared to chloroform, while Dr. Wiswall has found an increase of about 0.8. Analogous increases are evident in the solution values of 2,2-dichloropropane, 1,1-dichloroethane and 1,1-dichloropropane[10] as compared to the moment of methylene chloride, the increases again being a little larger than the estimated and the replacement of hydrogen by ethyl increasing the moment by slightly more than the replacement of hydrogen by methyl. The quantitative treatment of these increases in moment is too approximate to establish induction as the only cause of the increases, but, qualitatively speaking, it seems to be sufficient to be the cause.

A semi-quantitative application of the calculation of inductive effects to the moments of the fluorochloromethanes[11] gave excellent agreement between the observed values and those calculated on the assumption of 110° carbon valence angles. Although electron diffraction subsequently established the absence of any considerable distortion of these angles,[12] it also showed the existence of resonance with structures of the type  $H-\underset{H}{\overset{X^-}{C}}=X^+$ contributing to the structures of the molecules. The large moment that this structure must have would lead one, at first thought, to look for moments in these compounds abnormally high in comparison to those of the chloromethanes. If the two X atoms are the same halogen, the contribution of the structure  $H-\underset{H}{\overset{X^+}{\overset{\|}{C}}}X^-$ would equal that of the form given above and the halogen charges would thus cancel one another, the only effect of this resonance upon the moment being the slight change, presumably a decrease, due to shortening of the carbon–halogen distance. It is concluded from the interatomic distances that the $F^-C{=}Cl^+$ interaction[13] gives 5% double-bond character to the C–Cl bonds and that chlorine has about one-half the power to form double bonds that fluorine has, a statement which will be referred to again in connection with the resonance in the halogenated benzenes. This indicated predominance of the contributions of the polar structures with positive fluorine and negative chlorine over those of the structures in which the charges are reversed should tend to increase the observed moments. Because of the necessarily approximate evaluation of the effect of induction, such increases could be observed only if they were large. For example, the moment 0.45 of $CFCl_3$ might arise in large part from the greater contributions of structures such as  $F^+{=}\underset{Cl}{\overset{Cl}{C}}\ Cl^-$ as compared to those from structures such as  $F^-\ \underset{Cl}{\overset{Cl}{C}}{=}Cl^+$, since the moments of methyl fluoride and methyl chloride differ by only 0.04. If such resonance were the major cause of the moment, the moment

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[10] Gross, *Physik. Z.*, **32**, 587 (1931).

[11] Smyth and McAlpine, *J. Chem. Phys.*, **1**, 190 (1933).

[12] Brockway, *ibid.*, **41**, 747 (1937).

[13] Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 236.

of CF_2Cl_2, in which electron diffraction shows a greater shortening of the C–F distances and, therefore, greater contributions from structures with positively charged, double-bonded fluorine, should show a considerable increase over that of $CFCl_3$. The fact that the moment value 0.51 of CF_2Cl_2 exceeds that of $CFCl_3$ by just the 15% calculated from the tetrahedral structures of the molecules indicates that the effect of resonance on these moments is too small to be detectable. Study of the effect is complicated by the fact that the dipole due to resonance should have its positive end toward the fluorine side of the molecule, while the dipole arising from difference in induction effects should have its negative end toward the fluorine side of the molecule. The amount of resonance occurring in the fluorochloromethanes appears to be somewhat lower than that in the vinyl halides and halogenated benzenes, which will be discussed later and the effect of the resonance upon the moment depends mainly on the excess of the contribution of the form with positively charged fluorine over that with negatively charged fluorine, while, in the vinyl halides and halogenated benzenes, all the important polar structures have dipoles with their positive ends on the halogen. It is evident, therefore, that the moments of the fluorochloromethanes should be affected much less by resonance than those of the latter molecules and, indeed, the effects should, probably, be so small as to be obscured by those of induction.

In the discussion of the moments of the alkyl halides, the inductive effect of the primary carbon–halogen dipole upon the hydrocarbon chain has been shown to be sufficient to account for the differences in moment among the different chlorides and the effect of the chain upon the primary moment has been disregarded. The effect of small atomic charge differences on reaction rates has been shown by Ri and Eyring.[14] The decrease in stability of the halides on going from primary to secondary to tertiary suggests, although it does not necessitate, the possibility of differences in the carbon–halogen moments, but the differences must be extremely small since the difference of 0.04 between *n*-butyl and *t*-butyl chloride in Table I is slightly smaller than, but only a little different from what would be expected of the effects of the C–Cl dipoles upon the two hydrocarbon groups. The value 1.78 found for the C–Cl bond length in *t*-butyl chloride[15] differs from the normal value 1.76 by less than its probable error. The Raman frequency corresponding to the longitudinal carbon–chlorine vibration in the alkyl chloride[16] shows a rough analogy to the dipole moment in its variations and the binding constant calculated from it seems to parallel the chemical stability of the bond. However, mass effects influence this frequency and steric effects influence the chemical stability. One can only conclude that any change in the primary carbon–chlorine bond moment with change in the attached alkyl group is so small as to escape detection in these investigations.

As it is thought that the energy of an H–C bond on a tertiary carbon atom may differ considerably from that of an H–C bond on a primary carbon atom,[17] and as a rough relation between bond energy differences and dipole moments has been indicated,[8,18] it has seemed possible that isobutane might have a dipole moment of the order of 0.2×10^{-18} because of difference in moment between the H–C bond on the tertiary carbon atom and the other H–C bonds which are all on primary carbon atoms. The experimental investigation of this problem by Dr. R. H. Wiswall in this laboratory was unsuccessful because of the difficulty in removing impurities from the isobutane. However, the fact that Groves and Baker[19] have found zero moment for isopropylcyclohexane, which has one H–C bond on a tertiary carbon, as also for methyl, ethyl, and *t*-butylcyclohexane, indicates that any difference in the moment of this H–C bond must be extremely small. The zero moments found for many branched chain hydrocarbons could be cited in support of this conclusion, but their evidence is somewhat less conclusive because of their measurement in the liquid state. It is quite possible that the apparent difference in energy of this H–C bond on a tertiary carbon atom from that of the H–C bond on a primary carbon may arise from steric effects involving no detectable charge shift.

One would anticipate that the moment of the H–C bond in hydrogen cyanide would be larger than that of an H–C bond in a hydrocarbon because hydrogen cyanide, although a very weak acid, has a certain tendency to lose a proton. However, methyl cyanide has a much larger mo-

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[14] Ri and Eyring, *J. Chem. Phys.*, **8**, 433 (1940).

[15] Beach and Stevenson, THIS JOURNAL, **60**, 475 (1938).

[16] Harkins and Haun, *ibid.*, **54**, 3920 (1932).

[17] Taylor and Smith, *J. Chem. Phys.*, **8**, 543 (1940).

[18] Ref. 13, p. 68.

[19] Groves and Baker, *J. Chem. Soc.*, 1144 (1939).

TABLE II

DIPOLE MOMENTS (× 10^{11}) OF CHLORIDES CONTAINING FOURTH GROUP ELEMENTS AND HYDROGEN, ETHYL OR PHENYL GROUPS

$(CH_3)_3CCl$	2.15	$(C_6H_5)_3CCl$	1.95	$(CH_3)_2CCl_2$	1.99
SiH_3Cl	1.28			SiH_2Cl_2	1.17
GeH_3Cl	2.03	$(C_6H_5)_3GeBr$	2.5	GeH_2Cl_2	2.21
$(C_2H_5)_3SnCl$	3.44	$(C_6H_5)_3SnCl$	3.30	$(C_2H_5)_2SnCl_2$	3.85
$(C_2H_5)_3PbCl$	4.39	$(C_6H_5)_3PbCl$	4.21	$(C_2H_5)_2PbCl_2$	4.70

ment 3.94 than hydrogen cyanide 2.93, just as methyl chloride has a much larger moment 1.87 than hydrogen chloride 1.04. In their calculations of induction effects, Groves and Sugden[7] have obtained a value 3.00 for the moment of the cyanide group in methyl and ethyl cyanide. If this were correct and the cyanide group in hydrogen cyanide had the same moment, as it should have approximately, the H–C moment in hydrogen cyanide, instead of being larger than that in the hydrocarbons, would be negative, which seems impossible. It seems much more probable that the calculated cyanide moment value is too high and that the H–C moment value in hydrogen cyanide is small and close to that in the hydrocarbons. Similarly, the slight difference in the moments of acetic acid and methyl acetate shows the absence of any large abnormality in the H–O bond moment in spite of the considerable ionizing power of the acid.

It has been pointed out in previous work[20] that, if the bond moments depended wholly on intrinsic electronegativities of the bonded atoms and were uninfluenced by induction, resonance effects and possible unknown factors, the moments of molecules with four atoms or groups tetrahedrally arranged around a central atom should be independent of the nature of the central atom and should depend simply on the differences in electronegativity of the attached atoms. The reasons for the great departure of the moments of such molecules from the mere differences in electronegativity have been previously discussed,[6,8,20] but recent moment determinations in this laboratory by Dr. G. L. Lewis on many alkyl lead halides and by Mr. P. F. Oesper on phenyl lead halides, triphenylgermanium bromide and triphenyltin chloride have so extended the available experimental information on the subject as to warrant further discussion. Table II lists the moments available from these measurements or from the literature for the compounds in which one or two chlorines and three or two hydrogens, ethyl groups or phenyl groups are attached to the four corners of a tetrahedron with carbon, silicon, germanium, tin or lead at the center. Triphenylgermanium bromide is listed as the chloride has not been measured and the difference between them would not be large. We are essentially concerned with the monochlorides, but the dichlorides are listed as confirmatory evidence. In the absence of inductive effects, the tetrahedral structure should give these dichlorides moments 15% higher than those of the monochlorides. The lowering of their moments by induction and the decrease of this lowering with increasing size of the central atom and consequent increasing separation of the inducing dipoles has already been pointed out.[20] As values determined in solution have been used for all the substances except SiH_3Cl, SiH_2Cl_2, GeH_3Cl and GeH_2Cl_2, small discrepancies may arise from solvent effects. Also, there are unusually large experimental errors in the triphenylgermanium bromide measurements and in the lead compound measurements because of low solubility and conductance of the solutions. From what has already been said, it will be evident that the replacement of the hydrogens in SiH_3Cl, SiH_2Cl_2, GeH_3Cl and GeH_2Cl_2 by alkyl or phenyl groups would raise their moments, but the increases would not be sufficient to alter materially their magnitudes relative to those of the other moments in the table.

The drop in moment from the carbon to the silicon compounds has been explained already[21,22] as due, in part at least, to resonance with contributions to the structure from structures such as $H_3Si^-{=}Cl^+$, these contributions diminishing on going from silicon to germanium to tin compounds as shown by electron diffraction measurements. Brockway and Coop[21] have attributed the increase in moment with increasing polarizability and electropositive character of the central atom Z to a greater effect of these two factors upon the large Z–Cl moment than upon the smaller Z–C moment. As the moments of the monochlorides written in terms of bond moments

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[20] Smyth, Grossman and Ginsburg, THIS JOURNAL, **62**, 192 (1940).

[21] Brockway and Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938).

[22] Lewis and Smyth, THIS JOURNAL, **61**, 3063 (1939).

are (H–Z) + (Z–Cl) or (H–C) − (Z–C) + (Z–Cl) and of the dichlorides are 1.15 times this, the effect of such a greater increase of (Z–Cl) as compared to (Z–C) or (Z–H) is evident. If, however, the bond moment is approximately equal to the electronegativity difference between the two bonded elements as seems to be true in the case of bonds between hydrogen and other elements,[8] this increase must be attributed to inductive effects of the bond dipoles upon the central atom Z, but, when Z is more positive than C, the inductive effects of the Z–C dipoles oppose those of the Z–Cl dipoles and an increase in one should be partly cancelled by an increase in the other. Of course, differences in the locations of these idealized point dipoles relative to the polarizable matter may and, apparently, do alter the relative sizes of the inductive effects. Agreement between the bond moments and the electronegativity differences calculated from thermal data[23] tends to be better when, at least, one of the bonded atoms is small in size, which means that it has small polarizability.

The difference in electronegativity as calculated from thermal data depends upon the energy of separation of the positive and the negative electricity, which also give rise to the dipole moment associated with the bond between the two atoms in question. If, instead of being idealized as a point dipole of moment μ, the charge distribution is treated as $+e$ on one nucleus and $-e$ on the other giving rise to dipole moment $\mu = ed$, where d is the internuclear distance, it is evident that the energy of separating the charges and, hence, the calculated electronegativity difference should be proportional to e^2/d. Change in atomic size may, therefore, affect a bond moment in a manner very different from that in which it affects the electronegativity difference calculated from thermal data. Professor Henry Eyring, who pointed out this relationship to the writer, has found that the discrepancies between bond moments and thermal effects are actually greatly increased by the attempt to apply this relationship between them. It has been shown[6] that there is no apparent reason for the closeness of many of the actual numerical values of the bond moments to those for the electronegativity differences, although a rough parallelism should exist. Disagreement between the two sets of values and departure from this parallelism tends to increase with increasing atomic size, the bond moment tending to become larger than the electronegativity difference. This rough tendency is explicable in terms of the effect of increasing interatomic distance in tending to decrease the energy of separation of the charges and, hence, the calculated electronegativity differences. The failure to find any general quantitative expression for this effect probably arises from the treatment of the charge distribution as $+e$ on one nucleus and $-e$ on the other, when it may more nearly approximate several dipoles, the resultant of whose moments is the observed moment. Those of the dipoles which were relatively remote from one another would add to the resultant bond moment without greatly increasing the energy of charge separation.

Except in the case of the silicon compounds and, to a lesser extent, the germanium compounds, the lowering of the Z–Cl bond moment by contributions from doubly-bonded forms is small. Subtracting a rough correction of 0.3 for the H–C bond moment from the moment values of the monohalides in Table II gives values which should be lower limits for the Z–Cl bond moments, including the inductive effects in Z and the relatively small inductive effects in the hydrocarbon groups, which should be of the same order as the H–C moment. The values should be lower limits because the unknown Z–C moments oppose the Z–Cl moments, leaving the observed molecular moment as the resultant except for the small effects just mentioned. It has been pointed out[6] that even the lower limit 3.1 of the Sn–Cl bond moment is 60% as large as the moment of the sodium iodide molecule, in which the valence is typically electrovalent. The lower limit 4.1 calculated for the Pb–Cl bond is close to the value 4.9 for the sodium iodide molecule and about two-thirds that of the potassium chloride molecule 6.3, indicating that the Pb–Cl bond in this molecule has a large amount of ionic character. This is in accordance with the high melting points, low solubilities of the compounds in benzene, and appreciable conductance of their benzene solutions. It is interesting to note that the increase in ionic character in the Z–Cl bonds with increase in the size of the atom Z in these compounds parallels Fajnas' rule that the ionic character of an electrovalent bond increases with increasing size of the cation. It may be mentioned that the corresponding increase in covalent character with increasing size of the anion is shown in the decreasing moments

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(23) Ref. 13, p. 64.

of the hydrogen halides from HCl to HBr to HI, but tends to be obscured in more complicated molecules by the effect of increasing bond length and the induction effects which have been discussed.

The lower limit 4.1 found for the Pb–Cl moment is larger than the largest difference in Pauling's electronegativity values[23] 3.3 calculated between the most positive element, cesium, and the most negative, fluorine. The electronegativity difference 1.5 between sodium and iodine corresponds, according to Pauling's curve for the amount of ionic character against electronegativity difference,[24] to 43% ionic character in the Na–I bond in sodium iodide. The sodium–iodine distance in the molecules of the vapor has been found by electron diffraction measurements[25] to be 2.90 Å. If this molecule consisted of two undistorted ions, its moment should be $4.80 \times 10^{-10} \times 2.90 \times 10^{-8} = 13.9 \times 10^{-18}$. If it is assumed that the ionic character of the bond is wholly responsible for the moment, the amount of ionic character of the Na–I bond in the sodium iodide molecule is given by the quotient of its observed moment 4.9×10^{-18} divided by this calculated value 13.9×10^{-18}, which is $4.9/13.9 = 35\%$ ionic character as compared to 43% estimated from the curve. Similar calculations give results for the K–I and K–Cl bonds and for the Ge–Cl, Sn–Cl, and Pb–Cl bonds which are summarized in Table III.

TABLE III

AMOUNTS OF IONIC CHARACTER IN BONDS CALCULATED FROM DIPOLE MOMENTS AND FROM ELECTRONEGATIVITIES

Bond	$\mu_{\text{obsd.}}$	μ_{ionic}	Electroneg. difference	% Ionic from μ	% Ionic from Electroneg.
Ge—Cl	>2.0	10.6	1.3	>19	35
Sn—Cl	>3.1	11.5	1.3	>27	35
Pb—Cl	>4.1	12.1		>34	
Na—I	4.9	13.9	1.5	35	43
K—I	6.8	15.5	1.6	44	47
K—Cl	6.3	13.4	2.2	47	70

With the exceptions of the K–Cl bond, the moment of which, like those in the other two salts, is subject to large error because of its determination by the molecular beam method,[26] and the Ge–Cl bond, the moment of which is somewhat lowered by a very small amount of double bond character, the two methods give adequate agreement, as they should since the amount of ionic character in the hydrogen–halogen bonds given by dipole moments was used by Pauling to establish the relation between amount of ionic character and electronegativity difference. It seems probable that the greater lowering of the Ge–Cl bond moment by double bond character is insufficient to account for the entire difference in the amounts of ionic character in the Ge–Cl and Sn–Cl bonds, but rather that germanium is a slightly less positive element than tin, in contrast to the identical electronegativity values given by thermal data for the two elements.

This approach to the resonance of the bond which has been used by Pauling and in obtaining the results in Table III assigns all the dipole moment to the contribution of the ionic structure, which is treated as undistorted, and tacitly assumes that the covalent structure makes no contribution to the moment. Wall,[27] in a more rigorous treatment of the hydrogen halides, has assumed the moment of the covalent structure to be zero. This is in contrast to the equation of Mulliken[28] used by the writer in rearranged form, which contained a "homopolar dipole term." As we have not as yet any means of determining separately the "homopolar dipole term" or the covalent structure moment and the secondary moment induced in the non-bonding electrons, the moment will be tentatively treated in our further considerations as arising wholly from the contributions of rigid ionic structures. This approach, which has given moderately consistent results in Table III, will now be applied to an examination of the determination of the amount of double bond character by means of dipole moments as compared to bond lengths.

In order to show the magnitude of the errors involved in the calculation of the amount of double bond character x from bond length as given by electron diffraction measurements, the values of x thus calculated for carbon–halogen bonds by means of Pauling's table[29] from the bond lengths tabulated in the literature,[30,31] together with their probable errors calculated from those of the bond lengths, are given for a number of substituted benzenes in Table IV.

The only monohalogenated benzene for which reliable data are available is chlorobenzene, but as the variation of x with variation in the number

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(24) Ref. 13, p. 70.

(25) Maxwell, Hendricks and Mosley, *Phys. Rev.*, **52**, 968 (1937).

(26) Scheffers, *Physik. Z.*, **35**, 425 (1934).

(27) Wall, THIS JOURNAL, **61**, 1051 (1939); **62**, 800 (1940).

(28) Mulliken, *J. Chem. Phys.*, **3**, 573 (1935).

(29) Ref. 13, p. 175.

(30) Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

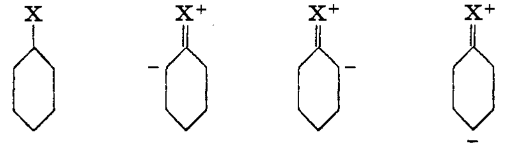
(31) Beach, *Pub. A. A. A. S.*, No. 7, p. 88 (1939).

TABLE IV

AMOUNTS OF DOUBLE BOND CHARACTER x IN CARBON-HALOGEN BONDS IN SUBSTITUTED BENZENES

	x
C_6H_5Cl	0.15 ± 0.05
o-$C_6H_4Cl_2$	.10 ± .06
m-$C_6H_4Cl_2$	.15 ± .09
p-$C_6H_4Cl_2$	.15 ± .09
1,3,5-$C_6H_3Cl_3$	.15 ± .09
C_6Cl_6	.12 ± .07
p-$C_6H_4Br_2$	.05 ± .04
1,3,5-$C_6H_3Br_3$	.05 ± .04
p-$C_6H_4I_2$	.18 ± .10
1,3,5-$C_6H_3I_3$	.10 ± .07

of halogens is well within the experimental error, an average of the values for the polysubstituted compounds may be used for bromobenzene, iodobenzene, and even for chlorobenzene in Table V for comparison with the values calculated from the dipole moments. These latter are calculated by equating the weighted mean of the moments of the principal individual contributing structures to the observed moment and solving the equation for x. The principal structures, their moments, and the amount, expressed in terms of x, which each is assumed to contribute to the structure are as follows:



	m_1	m_2	m_2	m_3
I.	$1 - x$	$1/3x$	$1/3x$	$1/3x$
II.	$1 - x$	$0.4x$	$0.4x$	$0.2x$

x is obtained by solving the equation I, $\mu = (1 - x)m_1 + 2/3xm_2 + 1/3xm_3$, or II, $\mu = (1 - x)m_1 + 0.8xm_2 + 0.2xm_3$, where μ is the moment observed for the compound in the vapor state or, in the case of iodobenzene, estimated for the vapor state from its solution value, and m_1 is taken as equal to the moment observed for the corresponding t-butyl halide, in which the inductive effect should be close to that of the monohalogenated benzene. The moment of t-butyl fluoride, which has not been measured, is estimated from consideration of the moments of methyl and ethyl fluoride[2] and the values for other halides in Table I to be 2.05. It is not unreasonable to assign equal contributions to each of the three polar forms as in equation I but, as each of the two ortho forms might contribute more than the para, their contributions are made double that of the para in equation II in order to observe the effect of changing the relative amounts of the contributions of the polar forms. The results obtained by means of equations I and II are listed in Table V in the columns headed correspondingly I and II.

TABLE V

AMOUNTS OF DOUBLE BOND CHARACTER x IN THE CARBON-HALOGEN BONDS IN THE MONOHALOGENATED BENZENES

	From: Bond lengths	Moments I	Moments II
C—F		0.036	0.040
C—Cl	0.14	.030	.033
C—Br	.05	.032	.035
C—I	.14	.040	.044

It is unfortunate that the accuracy of the electron diffraction measurements is not sufficient to distinguish different degrees of resonance existing in the different chloro-, bromo- and iodobenzenes, for, in the cases of the dipole moments, the effects of resonance cancel one another in the symmetrically substituted compounds, are practically independent of one another in the meta compounds, and are obscured by the effects of induction in the ortho compounds. It is evident that doubling the ratio of the contribution of the polar ortho structure to that of the para structure has only a small effect upon the calculated amount of double bond character. Indeed, complete exclusion of the para polar structure in chlorobenzene raises the calculated amount of double bond character only to 0.038. It seems improbable that the contribution of the para structure should be increased beyond that used in equation I and, if it were, the discrepancies between values of x calculated from bond lengths and those from moments would be increased. In the case of the C–Br bond, the agreement between the values calculated from moment and from bond length is as good as could be expected in view of the errors shown in Table IV. The amount of double bond character calculated for the C–I bond from bond length exceeds that calculated from moment by an amount greater than its probable error, but the large discrepancy could still conceivably arise from experimental error. The slightly larger discrepancy in the case of the C–Cl bond, the length of which is more accurately determined than are those of the C–Br and C–I bonds, is definitely too large to arise from experimental error. Although the calculation of the amount of double bond character in the C–F bond in fluorobenzene from dipole moments is less accurate than those for the other bonds because of the small uncertainty in moment value estimated for *t*-butyl fluoride, it appears almost certain that this C–F bond has somewhat more double bond character than the corresponding C–Cl bond, but not as much more as would be expected from the previously mentioned conclusion, based on the interatomic distances in fluoromethanes, chloromethanes and fluorochloromethanes that chlorine has about one-half the power to form double bonds that fluorine has.[13]

Hugill, Coop and Sutton[32] have made similar calculations, but have assumed that the moments of the contributing polar structures are reduced by induction and have used for their values 0.6 of the algebraic sum of the moment of the undistorted structure and the primary moment, for which the *t*-butyl halide moment has been used in these calculations. This reduction in the moments assigned to the polar structures increases the calculated amount of double bond character by an amount too small to alter materially the large discrepancies evident in Table V. These investigators have, however, greatly reduced, but not eliminated, the discrepancies by using the smaller moment values obtained by Groves and Sugden[7] by correcting for induction. They have further found that the use of the polar structure moments arbitrarily corrected for induction by the factor 0.6 gives amounts of double bond character for the carbon–halogen bonds in vinyl chloride, bromide and iodide and in chloro- and bromoacetylene which are in quite satisfactory agreement with the values calculated from bond lengths. The basis for the use of this factor 0.6 is the attribution to inductive distortion of the difference between the observed moments of the alkali metal halide molecules in Table III and those calculated for the pure undistorted ionic structures and a somewhat similar difference between a rough moment value observed for trimethylamine oxide in very dilute solution and the value calculated on the basis of a pure ionic bond between the nitrogen and the oxygen. As previously indicated, the difference in the case of the alkali metal halides may be treated in terms of the contributions of pure covalent and undistorted ionic structures as may that in trimethylamine oxide, which has been shown by recent accurate work[33] to be smaller than supposed by Hugill, Coop and Sutton, the observed nitrogen–oxygen bond moment being 4.4, slightly more than 0.6 of the calculated value for the undistorted ionic structure 6.5. In these structures on which the value of the factor 0.6 is based, the ionic charges are on immediately adjacent atoms in contrast to the structures of the halogenated benzenes where they are on atoms separated from each other by one other atom in the ortho structures and by three atoms in the para structures. There is an, at least formal, analogy between these structures and those of the dipolar ions for which Wyman[34] has calculated from experimental data approximate moment values in rough agreement with those calculated as the product of the ionic charge and the distance separating the positive and negative charges.

It may be concluded that the amounts of contributions of polar structures through resonance calculated from dipole moments tend to be lower than those calculated from interatomic distances, although the differences may be reduced by the assumption of inductive distortion of the polar structures. Although the absolute values of these contributions calculated from moments are uncertain because of the uncertainties underlying the fundamental approach to the treatment, their relative accuracy for molecules of more or less similar character is considerably greater than that of the values obtained from interatomic distances, as the differences in moment caused by resonance are usually much greater than the differences in interatomic distances.

The writer wishes to thank his co-workers, Dr. R. H. Wiswall, Dr. G. L. Lewis, and Mr. P. F. Oesper for the use of the dipole moment values which they have determined.

Summary

Dipole moments determined in the vapor state for alkyl chlorides and nitroparaffins are used together with those already in the literature to extend or strengthen previous conclusions as to the extent of inductive effects in straight and branched carbon chains. Differences in chemical reactivity between halogens or hydrogen on primary, secondary and tertiary carbon atoms are not reflected in detectable differences in moment.

The contributions of polar structures containing doubly-bonded halogen to the molecular structures of fluoromethanes and fluorochloromethanes should not greatly affect their moments. The effects of these contributions upon

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(32) Hugill, Coop and Sutton, *Trans. Faraday Soc.*, **34**, 1518 (1938).

(33) Linton, THIS JOURNAL, **62**, 1945 (1940).

(34) Wyman, *Chem. Rev.*, **19**, 213 (1936).

the moments are obscured by those of induction.

Dipole moments measured in solution for halides containing lead or germanium are used to calculate minimum values for the Pb–Cl and Ge–Cl bond moments. These, together with a previously calculated Sn–Cl moment, and the moments of the sodium iodide, potassium iodide, and potassium chloride molecules are used to calculate percentages of ionic character in the bonds in fair agreement with percentages calculated from electronegativities obtained from thermal data.

The dipole moments of the four mono-halogenated benzenes are used to calculate the fractions of double bond character in the carbon–halogen bonds in these molecules. The results are lower than those obtained from the carbon–halogen bond lengths given by electron diffraction. It is concluded that the absolute accuracy of the amounts of resonance contributions calculated from dipole moments is uncertain, though, in some cases, at least, the values are close to those given by interatomic distances. However, the relative accuracy of values obtained from moments for more or less similar substances is greater than that obtained by the use of interatomic distances.

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Photographic Fourier Syntheses*

BY MAURICE L. HUGGINS

Introduction

Electron density projections and Patterson interatomic distance vector projections—both types obtained by Fourier series summation—are becoming increasingly useful in studying the structure of crystals. Yet, although various ingenious devices have been utilized for speeding up the process, these summations are still quite laborious and time-consuming. A faster and more automatic method for obtaining a desired projection from the appropriate set of structure factors would therefore be highly desirable.

In 1929, W. L. Bragg[1,2] described an interesting optical and photographic method for making a Fourier summation from crystal diffraction data, the final result being a photograph representing semi-quantitatively the projected electron density distribution over one or more unit cells.

The present paper describes an extension of Bragg's method. It will be shown how the procedure can be made more automatic and much faster and how the results can be made more quantitative.

The Method

In principle, the method is very simple. Successively, onto a single photographic film or paper, exposures are made—one for each F_{hk0} value—in which the product of light intensity at a point x,y times the time of exposure is given by the equation

$$E_{hk} = I_{hk}t_{hk} = K_1[|F_{hk0}| + F_{hk0}\cos 2\pi(hx/a + ky/b)] \tag{1}$$

Here, h and k are the indices of the X-ray reflection concerned, a and b are unit distances on the projection, and k_1 is an arbitrary proportionality constant, the same for all the exposures. For the total exposure

$$E = \Sigma E_{hk} = K_1\Sigma|F_{hk0}| + K_1\Sigma F_{hk0}\cos 2\pi(hx/a + ky/b) \tag{2}$$

The second term on the right side of Equation (2) represents the desired density distribution. The first term, $K_1\Sigma|F_{hk0}|$, produces an unwanted uniform background over the whole photograph. This background, however, can, to a large extent, be eliminated, as will be shown.

Bragg projected through a single photographic plate, on which was a set of alternating light and dark bands, the transmitted light varying approximately in proportion to $(1 + \cos 2\pi nx)$ in the direction perpendicular to the bands. For each exposure, both the distance, r, from the plate in the projector to the projection paper and their relative orientation were suitably changed. The exposure time was made proportional to $r^2|F_{hk0}|$.

In the present technique, two separate films or "*hk* masks," in which the bands are properly spaced and oriented, are prepared, once for all, for each pair of *hk* values. (One is for use when F_{hk0}

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(1) W. L. Bragg, *Z. Krist.*, **70**, 475 (1929).

(2) W. L. Bragg, "The Crystalline State," The Macmillan Co., New York, N. Y., 1934, p. 229.