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SOME APPLICATIONS OF ELECTRIC MOMENTS TO ELECTRONIC THEORIES OF VALENCE

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As most of the electronic theories of valence in their application to organic compounds involve the idea of polarity as a controlling factor, it would seem logical to use the measure of molecular polarity, that is, the electric moment of the molecule, as a means of examining the validity of the theories. In the hands of many workers with these theories, the signs of positive and negative charges and the circles or dots representing electrons have gradually lost all physical significance and become mere symbols of chemical behavior. To attempt to apply principles of electrostatics to test these molecular formulas would be idle. However, hypotheses which have been developed on the basis of physical laws lend themselves to examination in the light of the electric moments of the molecules to which they are applied, provided that the molecules are not too complex.[1] It is not generally possible to accept or reject unreservedly an hypothesis on the basis of the electric moment of the molecule of a single substance or even of three or four substances, although strong evidence pro or con may be obtained. One may, however, set definite physical limitations upon the polarities supposed by the hypotheses and, at the same time, consider the limitations of the electric moment as a criterion by which these hypotheses may be judged.

In view of the uncertainty and the rapidity of change in the hypotheses of atomic structure and our ignorance of the fundamental nature of the chemical bond, it is impossible to assign definite electronic arrangements to the atoms in a molecule. It is generally believed, however, that a single chemical bond involves a pair of electrons and the electrostatic effect of their charges is represented by picturing certain locations between the linked atomic nuclei as occupied by the electrons. The consideration of these locations makes possible the discussion of the distribution of the electricity in the molecule.

In an electrically symmetrical molecule the center of gravity of the electrons coincides with the electrical center of gravity of the positive charges and the molecule has no electric moment. If the electrostatically effective position of an electron is displaced through a distance d, an electric doublet is created and the molecule now possesses an electric moment equal to the electronic charge, $4.774 \times 10^{-10} \times d$. The symmetrical tetrahedral structure commonly ascribed to methane should have

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[1] For an explanation of electric moment and its relation to molecular structure, see Smyth, *Phil. Mag.*, **47**, 530 (1924); THIS JOURNAL, **46**, 2151 (1924).

no electric moment, but it is highly improbable that the unsymmetrical pyramidal structure attributed by Henri to methane should not possess a moment.[2] The relation of the theory of a pyramidal carbon atom to the electric moments of tetra-substituted methane molecules has been discussed by Weissenberg[3] and by Ebert and von Hartel.[4] As Sänger[5] has found zero electric moment for the methane molecule, the usually accepted picture of a symmetrical structure appears justified.

The theory of alternating polarities has received much adverse criticism on chemical grounds and the supposed physical evidence of alternation given by melting points, heats of combustion, etc., has been shown to afford no proof of any intramolecular alternation of polarity.[6] The theory as proposed by Cuy[7] requires that, even in the paraffins, the carbons of the chain should be alternately positive and negative. The difference in polarity between the two carbons in ethane should give rise to an electric doublet, but no moment is found for the ethane molecule.[8] Although, because of the alternation and consequent canceling of the polarities, there should be no building up of large moments in the higher members of the series, there should certainly be moments in the molecules of many and differences should exist between adjacent members. *n*-Hexane and *n*-heptane have been shown to be without moment,[9] as have also the other isomers of heptane and one octane. If any alternation in polarity occurred, it would be impossible that all of these molecules should be electrically symmetrical. Further evidence against an alternation in polarity is given by the absence of any difference in moment among the higher members of other homologous series to be considered presently.

The differences between the polarizations of the isomers of heptane were shown by Smyth and Stoops to be so small that the largest difference would, if due to but one pair of electrons, correspond to a displacement of the effective position of the charges of less than 3×10^{-11} cm. from a symmetrical location, that is, approximately 0.002 of the distance between the carbon nuclei in the chain. This distance was calculated as an upper limit for the displacement. Actually, such differences in polarization as were observed might easily occur without any lack of electric symmetry in the molecules. Hydrocarbon molecules may be resolved into various

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[2] Henri, *Chem. Rev.*, **4**, 189 (1927).

[3] Weissenberg, *Naturwissenschaften*, **15**, 662 (1927).

[4] Ebert and von Hartel, *ibid.*, **15**, 668 (1927).

[5] Sänger, *Physik. Z.*, **27**, 556 (1926).

[6] Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928); Carothers, THIS JOURNAL, **46**, 2226 (1924).

[7] Cuy, *ibid.*, **42**, 503 (1920).

[8] Smyth and Zahn, *ibid.*, **47**, 2501 (1925).

[9] Smyth and Morgan, *ibid.*, **50**, 1547 (1928); Smyth and Stoops, *ibid.*, **50**, 1883 (1928).

alkyl radicals to which it is customary to assign varying degrees of electronegativity. Thus Lucas, Simpson and Carter[10] state that, in propane, due to the fact that hydrogen exerts a stronger pull on electrons than methyl does, the electron pairs joining the central carbon to hydrogens are presumably not so firmly held by the carbon so that the polarities of all the carbon–hydrogen unions in propane are not the same, hydrogen joined to the secondary carbon being more negative than hydrogen joined to a primary carbon. If the carbon linkages are tetrahedrally arranged, this difference in the polarities would make the molecule electrically unsymmetrical. A greater effect should be produced at the central carbon of *n*-heptane, as the two propyl groups attached to it are supposed to be less electronegative than the methyl groups on the central carbon of propane, but *n*-heptane is found to possess no detectable moment. It is unnecessary to make any assumption of tetrahedral linkages in order to conclude that the differently distributed groups in the isomers of heptane would give rise to electrical unsymmetry if their supposedly different electronegativities actually involved appreciably different displacements of their bonding electron pairs. The previously given calculation shows how small these displacements must be, if they exist at all. The electrical behavior of the paraffins thus gives no support to the hypothesis that the alkyl groups possess electronegativities which vary with the distance of the binding electron pair from the α-carbon.

It would appear, however, that the attachment of very strongly electronegative groups to the alkyl radicals should cause greater electron displacements and accentuate the differences between the radicals. When the hydroxyl is attached to an alkyl radical to form an alcohol, a strong electric moment results. In considering the dielectric constants of methyl, ethyl and propyl alcohols, Thomson[11] has pointed out that the intense electric field due to the principal moment of the molecule might be expected to give rise by induction on the rest of the molecule to moments of the same sign as the original moment, thus increasing the moment of the molecule as a whole. The increase in the moment of the molecule due to these small moments resulting from electronic displacement would be greater, the greater the length of the carbon chain. What appeared to be evidence of such a small increase with increasing length of the carbon chain was obtained by the writer[1] in calculating the moments of several alcohols and in other series as well, but it now seems probable that, at least in the alcohols and ketones, the apparent small increase in moment with increasing size of the molecule was due to error caused by molecular association. The strong molecular association of the alcohols and water makes their moments difficult to determine with accuracy, but the most recent values

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[10] Lucas, Simpson and Carter, This Journal, **47**, 1462 (1925).

[11] Thomson, *Phil. Mag.*, **46**, 497 (1923).

lie within 0.15×10^{-18} of 1.7×10^{-18} and show no regular variation with increase in the length of the chain.[12] It is evident that there are no very great differences among the displacements of the bonding electron pairs in the different alkyl groups in the alcohols.

More satisfactory conclusions may be drawn from the moments of the halides, which are less affected by molecular association and are not complicated by the presence of two doublets in the molecule as is the case with the alcohols.

TABLE I

ELECTRIC MOMENTS OF THE HALIDES $\times 10^{18}$

	X = Cl		Br	I
HX	1.03(1)		0.79(1)	0.38(1)
CH_3X	1.59(2)			1.62(3)
C_2H_5X	1.98(2)		1.86(4)	1.66(5)
C_4H_9X	1.89(6)		1.87(6)	
$C_7H_{15}X$			1.86(6)	
C_6H_5X	1.52(4)		1.57(7)	
cis-CHX=CHX	1.85(8)		1.22(8)	0.75(8)
trans-CHX=CHX	0(4)		0(8)	0(8)
cis-CHCl=CHBr		1.54(8)		
trans-CHCl=CHBr		0(8)		
$CH_2=CCl_2$	1.18(8)			

(1) Zahn, *Phys. Rev.*, **24,** 400 (1924); (2) Sircar, *Indian J. Phys.*, **12,** 197 (1928); (3) Mahanti and Sen Gupta, *ibid.*, **12,** 191 (1928); (4) Smyth and Morgan, THIS JOURNAL, **50,** 1547 (1928); (5) Unpublished work of Dr. W. N. Stoops; (6) Unpublished work of Mr. H. E. Rogers; (7) Williams, *Physik. Z.*, **29,** 683 (1928); (8) Errera, *Physik. Z.*, **27,** 764 (1926).

In the molecules of these halides the negative end of the electric doublet is toward the halogen. Consequently, the more electronegative the group attached to the halogen, that is, the more strongly it draws the binding electron pair toward itself, the shorter is the distance between the centers of gravity of the positive and negative electricity and the smaller the moment. This works out quite satisfactorily for hydrogen, methyl and ethyl chlorides, in which the moment increases as the supposed electronegativity decreases. The difference between ethyl chloride and butyl chloride is no greater than the combined probable errors in the values. An accurate value for methyl bromide is lacking, but approximate values calculated by Höjendahl[13] show that the moment of methyl bromide is about 0.25×10^{-18} lower than that of ethyl bromide. The supposed differences in electronegativity of the bromides and iodides, as in the case of the chlorides, accord well with the increase in moment from hydrogen to ethyl. Beyond this, however, no difference is apparent in the

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[12] Stranathan, *Phys. Rev.*, **31,** 653 (1928); Krchma and Williams, THIS JOURNAL, **49,** 2408 (1927); Williams, *Physik. Z.*, **29,** 204 (1928).

[13] Höjendahl, "Thesis," Copenhagen, 1928.

chlorides and bromides, data for the iodides being lacking. The moments of chlorobenzene and bromobenzene are much higher than those of the corresponding hydrogen halides, although the phenyl group is supposed to be more electronegative than hydrogen. The supposedly different electronegativities are thus only partially successful in explaining the differences in moment. It is evident that some effect is transmitted through the first two carbons of a chain, although the effect upon the second is small and, beyond the second, no effect is apparent in the electric moment.

It is of interest to contrast this transmission of an electrical effect through a chain with the effect of the chain upon the ionization constants of unsubstituted and halogenated fatty acids as quoted by Lowry[14] and by Kharasch and Darkis and shown in Table II.

TABLE II

IONIZATION CONSTANTS OF FATTY ACIDS ($\times 10^5$)

		α			β			γ			δ		
		Cl	Br	I	Cl	Br	I	Cl	Br	I	Cl	Br	I
HCOOH	21.4												
CH_3COOH	1.8	155	156	75									
CH_3CH_2COOH	1.4	147	108	90	8.6	9.8	9.0						
$CH_3(CH_2)_2COOH$	1.5	139	106		8.9								
$CH_3(CH_2)_3COOH$	1.6							3.0	2.6	2.3			
$CH_3(CH_2)_4COOH$	1.46										1.9	1.9	1.7

The constants for the unsubstituted acids in the second column of Table II show that, as in the case of the electric moments of the halides, lengthening of the hydrocarbon chain beyond two has little effect. The values for the halogenated acids are somewhat conflicting but, after a great drop in the effect upon the ionization when the halogen is moved from the first to the second carbon, the effect continues to diminish as the distance of the halogen from the carboxyl increases and is still noticeable in the δ-halogenated acid, where it has to be transmitted through five carbons and an oxygen. Yet, in the alkyl halides, no electronic shifts produced by halogen more than two carbons away can be detected by means of electric moments.

Wolf and Lederle[15] have found that the electric moments of a number of ketones, including methylhexyl ketone and methylnonyl ketone, differ from the value for acetone by no more than the experimental error. Their results give no evidence of any change in moment with increasing length of the hydrocarbon chain. There is thus no measurable electrostatic effect transmitted beyond the first carbons attached to the carbonyl group and no sign of any alternating polarity in the chains.

Electronic theories of valence have been applied very frequently to the double bond and, by many investigators, the bond between two carbon

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[14] Lowry, *Trans. Faraday Soc.*, **19**, 497 (1923).

[15] Wolf and Lederle, *Physik. Z.*, **29**, 948 (1928).

atoms has been regarded as polar, one pair of electrons being shared between the two carbons and one of the carbons containing one more pair of electrons than the other. Smyth and Zahn[8] have found the electric moment of the ethylene molecule to be zero and have therefore concluded that no more than a small proportion of the ethylene molecules, if any, can be polar. It was further concluded that a molecule in which a single unpaired electron was held by each carbon should possess a moment and therefore could not exist in any considerable quantity in the ethylene. This conclusion is supported by the recent discovery of Vaidyanathan[16] that ethylene is diamagnetic instead of paramagnetic as previously supposed. The zero moment found experimentally for ethylene does not disprove the theory of Lowry[17] and of Carothers[6] that a very small fraction of the molecules containing a double bond are polar at the bond and that it is this small fraction which is active. The small moment, 0.37×10^{-18}, found for α-butylene may be due to the difference in the electronegativities of the hydrogen on one side of the doubly-bonded carbons and the ethyl on the other side as the electrons of the double bond are shown by the high refraction associated with them to be mobile and more easily displaceable than those in a single C–C bond.[18] The moment may, however, as suggested by Smyth and Zahn, be due to small electronic shifts induced in the ethyl group by the force field around the double bond.

If the double bond consisted essentially of a single electron pair held between the atoms and a second pair held by one atom or the other, as supposed in most theories of a polar double bond, the difference in freedom of rotation between singly and doubly linked atoms would not be explained. This well-recognized difficulty, which has been discussed by Sidgwick,[19] is, of course, obvious in the problem of geometrical isomerism. The comparative rigidity of the double bond is brought out strikingly by the results of Errera for the moments of the acetylene dihalide molecules given in Table I, where the absence of moment in the *trans*-compound fits in admirably with the conventional representation of the double bond as formed by the sharing of an edge between two carbon tetrahedra. The doublets at the other imaginary tetrahedral apices thus brought into one plane would cancel one another in the *trans*-compounds so that the moments of the molecules would be zero. Any freedom of rotation about the bond would tend to produce electrical dissymmetry and a resultant moment, as found in ethylene chloride, bromide and glycol, for which large moments have been calculated approximately.[18] One might wonder

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[16] Vaidyanathan, *Indian J. Phys.*, **12**, 165 (1928).

[17] Lowry, *Trans. Faraday Soc.*, **19**, 488 (1923); *J. Chem. Soc.*, **123**, 822 (1923).

[18] See Smyth, *Phil. Mag.*, **50**, 361 (1925).

[19] Sidgwick, *Trans. Faraday Soc.*, **19**, 469 (1923).

why the *cis*-compounds with the two halogen doublets reënforcing each other on the same side of the molecule do not have larger moments than the alkyl halides where there is only one halogen doublet. As was found in the chloromethanes and the dihalogenated benzenes,[20] the two halogen atoms repel each other, widening the angle between the axes of their doublets and decreasing the resultant moment of the molecule as a whole. The repulsion and consequent widening of the angle should be greater, the larger the halogen atoms, and it is evident that the moment is increasingly reduced on passing from chlorine to bromine to iodine. Purely geometrical considerations show that, when the two halogens are attached to the same tetrahedral carbon, the angle between their doublets is greater and the resultant moment less, as evidenced in the value for $CH_2{=}CCl_2$.

The rigidity of the doublet bond between carbon atoms is maintained in the structure proposed by Kharasch and Darkis[6] in which two pairs of electrons are shared between the two carbons, one pair being close to the carbon to which the less electronegative groups are attached and a definite polarity being postulated. This is neither proved nor disproved by the moments in Table II, but the zero moment found for ethylene shows the absence of any detectable polarity in this simple molecule, while the postulates of Kharasch and Darkis would lead us to expect a marked polarity. There appears to be no physical foundation for the postulate of Kharasch and Darkis that "the relative position of the second pair of valence electrons of the double bond depends upon the nature of radical attached to it in such a way that they are always on the carbon atom opposite to that carrying the most electronegative radicals." The more electronegative radicals draw their binding electron pairs farther away from the carbon to which they are attached, thus increasing the effective nuclear charge of this carbon. The increased charge should tend to shift any other adjacent electrons toward this carbon and thus increase very slightly the effective nuclear charge of the carbon away from which they have shifted. A mechanism of this general character is commonly assumed to explain the transmission of an effect through a chain. The short distance through which such an effect can be detected electrostatically has been pointed out. The postulate of Kharasch and Darkis requires that the electrons be forced away from the carbon with the higher effective nuclear charge toward that with the lower charge. However effective such a postulate may be in explaining chemical behavior, it appears electrostatically unsound.

When the results of Errera, Smyth and Morgan and Höjendahl[21] for the moments of substituted benzenes were found to be consistent with

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[20] Smyth, *Phil. Mag.*, **47**, 530 (1924); Smyth and Morgan, THIS JOURNAL, **49**, 1030 (1927); Errera, (8) Table I.

[21] Höjendahl, *Nature*, **117**, 892 (1926).

the hypothesis of a benzene ring forming a plane hexagonal structure, it was thought that the relative electronegativities of radicals could be determined not only by comparing the electric moments of analogous compounds containing the different radicals but also by measuring the moments of molecules in which any two groups to be compared were placed opposite one another in the para-position.[20] Williams[22] has recently constructed a list showing the moments produced by the attachment of each of nine common radicals to the benzene ring. When two groups are in the para-positions, the resultant moment should be the difference of the two separate moments, the signs of the moments being taken into account. Although this relation has been found to hold approximately for many of the simple groups, marked deviations occur frequently when more complex groups are attached.[22,13] Particularly in the ortho- and meta-positions, the groups may attract or repel one another quite apart from their action through the carbons of the ring and the resulting effect upon the moment of the molecule is commonly much greater than any to be expected from electronic shifts in the carbon ring. The repulsive effects of this kind, which have been discussed by Smyth and Morgan[20] for the substituted benzenes, are similar to those occurring in the acetylene dihalides. Because of these large changes external to the ring, it seems useless at present to attempt to treat the possible small electronic displacements and polarities occurring within the ring.

Our consideration of electric moments has shown that alkyl groups do not differ sufficiently in electronegativity to cause any detectable electrical dissymmetry in saturated hydrocarbons. When a halogen atom is attached to a carbon chain, only the first two carbons are apparently affected electrostatically, the β-carbon but slightly. It may be supposed that the shifts of electron pairs induced by the strongly electronegative halogen, or, putting it in other terms, by the large doublet at the end of the chain, are too small, in the carbons beyond the first two, to have any measurable electrostatic effect. On the other hand, the ionization constants of the halogenated fatty acids in Table II show that the effect of a halogen is transmitted through five carbons and an oxygen. Moreover, the assumption of polarities arising from the different electronegativities of radicals appears to be useful in explaining and predicting chemical behavior. It is difficult to believe that polarities as small as they must be, if they exist at all, in the chains of the alkyl groups or in a symmetrically located double bond can have powerful directive influence or greatly affect chemical activity or degree of ionization. The moments of any doublets existing must be so small that they would exert considerable forces only at very short distances and, at these distances, the interatomic forces which vary inversely as a high power of the distance should be so large that one might

[22] Williams, *Physik. Z.*, **29**, 683 (1928).

expect the effect of the forces due to the possible minute polarities to be negligible in comparison. In a molecule there is a possibility of a great variety of energy levels, many of which may differ from one another too little to give rise to measurable differences in polarity between molecules in which these levels are differently occupied. Too little is known of these levels in simple atoms to permit of intelligent reasoning in regard to complex compounds, but one cannot but wonder if the effects transmitted through long chains and the varied chemical behavior attributed to variation in polarity are not due to changes and differences in the energy levels occupied by the valence electrons. Polarity may occur, but ordinarily as an accompanying result rather than as a determining factor in chemical behavior. Although pronounced polarity is doubtless a factor in chemical behavior, a large portion of the polarities assigned by the various electronic theories of valence must be regarded not as a physical fact but merely as a pragmatic representation of chemical behavior.

Summary

Electric moments are used as a test of those electronic theories of valence which require polarity in the molecule. The absence of electric moment in methane, ethane and the higher paraffins shows that there is no measurable alternating polarity in the hydrocarbon chain or inherent dissymmetry in the electron linkages of alkyl radicals. The absence of variation in the moments of the higher ketones and alkyl halides leads to the same conclusion and shows that in these carbon chains no measurable polarity is transmitted through more than two atoms.

The ethylene double bond has no measurable polarity, but when different radicals are attached on opposite sides of the bond polarity may occur. The absence of rotation about the double bond is evidenced by the difference in moment between the *cis* and the *trans* isomers of the acetylene dihalides.

It is suggested that the directive influences and effects upon chemical activity commonly attributed to differences in polarity may be due rather to differences in the energy levels occupied by the valence electrons, which may or may not give rise to measurable polarity.

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