[Contribution from the Department of Chemistry of Princeton University]

THE ELECTRIC MOMENTS OF THE MOLECULES OF MONOCARBOXYLIC ACIDS AND THEIR ESTERS

By Charles P. Smyth

Received April 13, 1925 Published July 3, 1925

In previous work[1] it has been assumed that each electron in an atom or molecule has an electrostatic effect equivalent to that which it would exert if located at some fixed point. In the lighter atoms, at least, the inner electrons which form the kernel of each atom appear to be so symmetrically arranged around the positive nucleus and so rigidly bound that little error is introduced by assuming that their center of gravity is permanently located in the nucleus. The effective locations of the outer electrons are assumed to be in pairs which, in the lighter atoms, lie at the apices of regular tetrahedra. This so-called pairing of electrons is consistent with the magnetic behavior to which Lewis[2] has recently called attention, for, if the orbits of two electrons are so placed as to attract each other magnetically and neutralize each other's magnetic effect, it is reasonable to treat their effective electrostatic positions as practically coincident.

The calculation of the locations in a molecule of the centers of gravity of these effective electrostatic positions and of the positive charges makes it possible to obtain the electric moment of the molecule, that is, the product of the charge at either center of gravity by its distance from the other center of gravity. It has been shown that the value calculated in this way for the moment of a molecule is usually two or three times as large as the value obtained from experimental data, unless account is taken of the shifts of the effective positions of the electrons from symmetrical locations because of forces acting within the molecule. These electronic shifts cannot be calculated with accuracy, but calculations based on atomic refractions show that their magnitude is sufficient to account for the difference between the calculated and observed values of the moment.

The relative sizes of the moments of several simple types of molecules have been satisfactorily explained by thus assuming the molecules to be made up of tetrahedra joined to one another by their apices. A small increase in moment with increase in the length of a hydrocarbon chain in a molecule has been attributed to secondary doublets induced in the chain by the principal doublet in the molecule, the number of secondary doublets being greater, the greater the number of displaceable electrons in the molecule, and it has been seen that the mutual repulsion of two or more groups attached to the same atom in a molecule may considerably

---

[1] Smyth, *Phil. Mag.*, **47**, 530 (1924); This Journal, **46**, 2151 (1924).

[2] Lewis, *Chem. Rev.*, **1**, 231 (1924).

affect the moment, the effect depending upon the bulk of the groups and the tendency of the binding electrons to maintain their symmetrical locations. This tendency, which is equivalent to an extreme localization of the valence forces on the imaginary surface of the atom, may be measured by a constant *f*, which is inversely proportional to the atomic refraction.

The molecules of the carboxylic acids and their esters are more complex structures than any hitherto studied in this manner. In Fig. 1 the structure of the acetic acid molecule is shown projected upon a plane of symmetry, which should contain the axis of the principal doublet of the molecule, the moment thus having no component perpendicular to this plane. The heavy black dots represent positive nuclei, and the small circles electrons. The two inner electrons adjacent to each nucleus are not shown, as their effect is supposed to be canceled by two of the positive charges of the nucleus. The two electron pairs forming the double bond of the carbonyl group are treated as lying at the ends of a shared tetrahedral edge which is bisected by the plane of the diagram. The hydroxyl and methyl groups are treated as free to rotate about the lines joining their oxygen and carbon nuclei to the nucleus of the carbonyl carbon, and their average electrostatic effects are calculated by projecting their charges on the extension of these lines. The locations found for the centers of gravity of the positive and negative charges are represented by the heavy enclosed signs, + and −, which, for convenience in representation, are shown on a scale ten times that of the rest of the diagram. Calculation has shown that a hydrogen nucleus may be replaced by a methyl group provided that the distances of the hydrogen nuclei from their bonding electrons in the methyl group are the same as was that of the original hydrogen from its bonding pair. Results on other classes of substances show that a hydrogen may be replaced not only by a methyl group, but also by a phenyl group without producing any appreciable

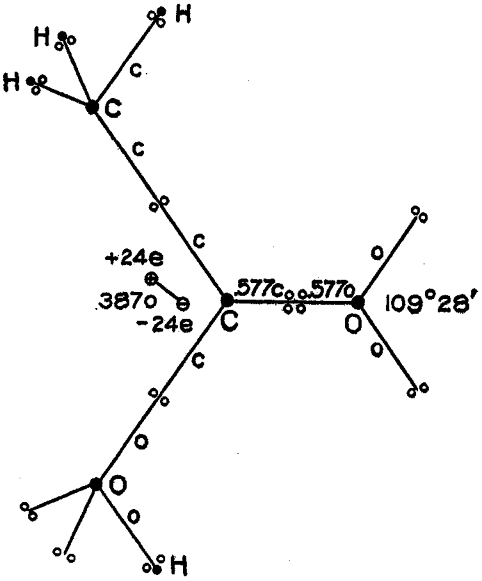

Fig. 1.—Structure of the acetic acid molecule. The actual distance between the centers of gravity of the positive and negative charges is 0.03870, one-tenth of the distance in the diagram.

change in moment other than the small differences resulting from induction or the altered repulsion of other groups in the molecule. All the unsubstituted monocarboxylic acids and their esters should thus have moments differing from each other only by the amounts due to the secondary effects mentioned. In order to simplify comparison with other types of molecules, we may, as an approximation, neglect the unknown distance of the hydrogen nucleus from its bonding pair, which is presumably small in comparison with o or c, the distance of this pair from its oxygen or carbon nucleus. The moment is then found to be $0.93\ o \times e$, where e is the electronic charge, 4.774×10^{-10} e.s.u., and a value of $1.155\ o \times e$ is obtained by the same simplified method for the ketones, aldehydes, alcohols, ethers and water, which have been shown to have moments differing from each other only because of the secondary effects of induction and mutual repulsion between the two groups attached to the oxygen atom.

TABLE I

ELECTRIC MOMENTS OF ACIDS AND ESTERS $\times 10^{18}$

$HCOOH$	1.35	CH_3COOH	1.30			$HCOOC_2H_5$	1.54
$HCOOCH_3$	1.37	CH_3COOCH_3	1.44	$C_6H_5COOCH_3$	1.53	$CH_3COOC_2H_5$	1.47
$HCOOC_2H_5$	1.54	$CH_3COOC_2H_5$	1.47[a]	$C_6H_5COOC_2H_5$	1.58	$C_2H_5COOC_2H_5$	1.51
$HCOOC_3H_7$	1.65	$CH_3COOC_3H_7$	1.53			$C_3H_7COOC_2H_5$	1.52
		$CH_3COOC_4H_9$ (*n*)	1.52			$C_4H_9COOC_2H_5$	1.54
$HCOOC_4H_9$(*i*)	1.74	$CH_3COOC_4H_9$ (*i*)	1.58	$C_6H_5COOC_4H_9$ (*i*)	1.68		
$HCOOC_5H_{11}$	(1.60)	$CH_3COOC_5H_{11}$	1.56	$C_6H_5COOC_5H_{11}$	1.69	CH_3COSH	1.55
		$CH_3COOC_6H_5$	1.38			CH_3COCl	1.70
$ClCOOCH_3$	1.62	$CHCl_2COOH$	1.70	$CH_2(CN)COOC_2H_5$	2.17	$CH_3CHBrCOOC_2H_5$	1.84
		$CHCl_2OOH$	1.39	$CHCl_2COOC_2H_5$	1.91		
		CCl_3COOH	1.25	$CCl_3COOC_2H_5$	1.82		

[a] At the boiling point $\mu = 1.62 \times 10^{-18}$.

In Table I are given the values of the electric moments of the molecules of a number of acids and esters calculated from data upon the specific refractions at two or more wave lengths, one or more values of the dielectric constant with the corresponding densities and temperatures, the molecular diameter, and certain universal constants.[3] The data, taken for the most part from Landolt-Börnstein "Tabellen" (5th edition), were determined at room temperature or at temperatures a little above the melting points.

The results for the acids are undoubtedly low because of molecular association in the liquids, and the values for the lower esters may be a little low for the same reason, as indicated by the fact that the value for ethyl acetate calculated from data obtained at its boiling point is 1.62 $\times 10^{-18}$, as compared with 1.47×10^{-18} at room temperature. When this value is compared with that of 2.08×10^{-18} for acetone at its boiling point, it is seen that the ratio of the former to the latter is $(1.62 \times 10^{-18})/(2.08 \times 10^{-18}) = 0.78$, as compared with the calculated ratio, $0.93/1.155 =$

---

[3] Compare Smyth, *Phil. Mag.*, **45**, 849 (1923).

0.81. In general, the observed ratio is somewhat less than 0.8, but the agreement is rather better than might be expected in view of the many complicating factors.

The formates, acetates and benzoates show an increase in moment with increase in length of the carbon chain of the alcohol radical because the principal doublets induce electronic shifts which are equivalent to small secondary doublets along the chain and, the greater the length of the chain, the greater the number of these doublets and, consequently, the greater the moment of the molecule as a whole. The ethyl esters, however, show no such increase in moment with increase in the length of the acyl carbon chain. Such behavior is readily understandable if the structures indicated by the X-ray measurements of Müller and Shearer[4] are correct. In Fig. 2, I represents the arrangement of the carbon atoms in the acyl radical of an ester molecule and II represents that in the alcohol radical, the carbon atoms in both cases being joined by electron pairs at shared corners of tetrahedra. If the carbon atoms are joined in the manner thus proposed by Müller and Shearer, the hydrogen nuclei which are attached to two apices of each carbon tetrahedron must lie, one above the plane of the paper, in which the carbon nuclei lie, and the other an equal distance below it, the two, together with their binding electron pairs, being projected upon the plane of the diagram. An electric doublet placed with its axis perpendicular to the axis of a carbon chain of either Type I or Type II will produce small shifts of the positive and negative charges relative to each other, equivalent to the formation of small electric doublets. In I, the doublets produced by the shift of the hydrogen nuclei and their binding electrons attached to two carbon atoms in the same horizontal plane support each other, but are opposed by equal

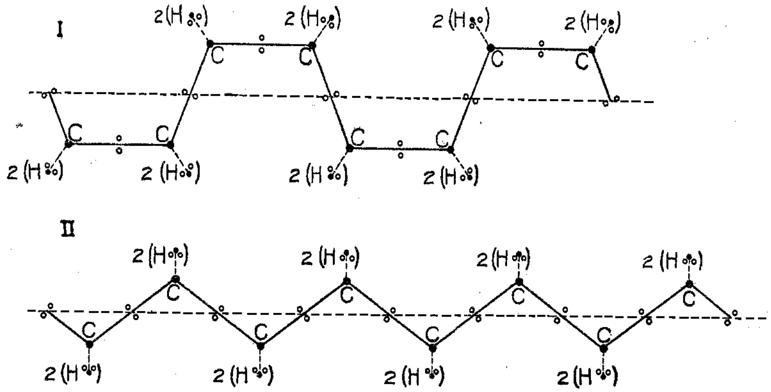

Fig. 2.—(I) Structure of the acyl radical of an ester molecule. (II) Structure of the alcohol radical of an ester molecule.

[4] Müller and Shearer, *J. Chem. Soc.*, **123**, 3156 (1923).

doublets induced in the opposite direction by the shift of the hydrogen nuclei and electrons attached to the next two carbons in the other horizontal plane. In II, a similar cancellation of effects occurs on successive carbons. In an odd numbered carbon chain, the doublets on one atom would be uncanceled, which should give a slightly higher moment for molecules containing a hydrocarbon chain with an odd number of carbons, but the effect would be much smaller than the usual experimental error. The only appreciable increase in moment would be due to the shift of the electrons shared between the carbon atoms, these small doublets all acting in the same direction. A doublet with its axis parallel to the axis of the carbon chain induces doublets in I, such that those on successive carbons oppose each other, the net result of all induction on a structure of Type I being only a very small increase in moment, as exhibited in the ethyl esters. However, in Structure II, charges of like sign will shift in the same direction parallel to the axis of the chain, so that the induced doublets will support and tend further to increase one another, the net result being an increase in the moment of the whole system with increase in the length of the chain as shown by the formates, acetates and benzoates. The behavior just described provides a possible physical basis for the theory of induced alternating polarity, since in the neighborhood of an electric doublet of appreciable size the carbon atoms in chains of this character would show a slight alternation in the intensities of their electrovalence forces.

Study of the ketones, alcohols and ethers has shown that, when a bulky group attached to a carbon atom shifts its position relative to that atom because of the repulsion by another attached group, the moment of the molecule is but slightly affected, while a similar shift of a group attached to an oxygen atom decreases the moment appreciably. The groups attached to the carbonyl carbon and the hydroxyl oxygen in the esters are so far apart that their mere bulk, unless very considerable, should not affect one another. However, the phenyl group in methyl benzoate and phenyl acetate is very bulky. If, in Fig. 1, the methyl group is replaced by a phenyl group and the hydroxyl hydrogen by a methyl group as in methyl benzoate, the phenyl group is probably displaced upward and to the right from its symmetrical position of attachment, a change which, because of a compensating shift of the binding electrons, should have little effect upon the moment of the molecule. In phenyl acetate, the phenyl group, which has replaced the hydroxyl hydrogen in Fig. 1, is displaced downward and to the right, which is equivalent in its effect to a similar displacement of the hydroxyl hydrogen but, because of the rigidity with which the oxygen electrons are bound, the accompanying electron shift is not sufficient to compensate for this change. The net result is the reduction of the distance of the center of gravity of the positive charges from that of the negative, which causes the decrease observed in the moment of phenyl acetate.

The value for the moment of thio-acetic acid is higher than that of the ordinary acid, perhaps, because of lower molecular association, which may play a more important part than the greater mobility of the sulfur electrons. If the acetyl chloride molecule were undistorted, it should have a moment only a little smaller than those of the aldehydes and ketones and somewhat greater than those of the unsubstituted acids and esters, but the moment is only a little larger than the values for the latter substances, probably because of the ease of displacement of the chlorine electrons. Calculation shows that replacement of a hydrogen in the acyl chain of the molecule by a halogen atom or cyanide group introduces a doublet which opposes the moment of the rest of the molecule. If no distortion and shifting of electrons occurred, the successive replacement of hydrogen atoms by chlorine would decrease the moment of the molecule as a whole until, in trichloro-acetic acid or a trichloro-acetate, its direction would be reversed. In monochloro-acetic acid the negative chlorine produces electronic shifts which oppose the calculated decrease in the moment of the molecule and, in particular, it attracts the hydrogen nuclei, drawing them upward and being itself drawn downward, thus raising the position of the positive center of gravity and lowering that of the negative, which is equivalent to increasing the moment. Incidentally, the drawing of the hydroxyl hydrogen nucleus toward the chlorine weakens its binding to the oxygen and so facilitates its splitting off to form an ion. This effect increases when a second, and then a third chlorine is substituted on the carbon, so that the strength of the acid increases. It is apparent that these influences not only counteract the decrease in moment which would result from the substitution if there were no distortion, but actually increase the moment of the monosubstitution products. When two or three chlorines are attached to the same carbon, the strong repulsion between them, due to their considerable bulk, causes a distortion which introduces a new factor into the situation. It is now quite possible that the increased shifts of the charges may not be sufficient to counteract the decrease in moment resulting from the increased number of negative groups.

The values for the three chloro-acetic acids are low because of molecular association, but show an increase from the unsubstituted acid followed by a decrease with increasing chlorine content. The value for methyl chloroformate, although somewhat uncertain is larger than that of the corresponding unsubstituted ester. No value is available for a monochloroacetate, and that for ethyl cyano-acetate is probably a little higher than that of the corresponding chlorine-substituted compound, because the moments of the cyanides have been found to be somewhat higher than those of the corresponding chlorides, while that of ethyl α-bromo-propionate is probably a little lower because the bromine compounds are ordinarily lower than the chlorine compounds. Ethyl di- and trichloroacetates show a decrease analogous to that exhibited by the acids. It is evident that the moment of a complex molecule is the resultant of several doublets which may, in part at least, oppose one another. The polarity of one part of a molecule, which may determine the tendency of the molecule to ionize, may be altogether different from the polarity of the whole molecule as indicated by the electric moment.

The fact that the variations among the electric moments of different molecules may be explained by the assumption of electron pairs shared between atoms, which tend strongly to maintain their effective positions in definite symmetrical locations in the molecules, seems to support the idea that valence forces are highly localized and directive in character, as indicated by the X-ray study of solids and the recent conclusions of Vorländer[5] upon liquid crystals.

Summary

1. The electric moments of the molecules of a number of monocarboxylic acids and esters are calculated from their structures, which are assumed to be formed by the linking of atoms by electron pairs symmetrically located at the apices of regular tetrahedra. The ratio of the moments thus obtained to those previously calculated for the molecules of the ketones, aldehydes and alcohols is in good agreement with that of the moments obtained from experimental data on these substances.

2. Differences in moment may arise from the mutual repulsion of bulky groups in a molecule and from differences between the structures of hydrocarbon chains as indicated by X-ray measurements.

3. Results on chlorine substitution products show that the polarity of one part of a molecule, which may determine the tendency of the molecule to ionize, may be altogether different from the polarity of the whole molecule as indicated by the electric moment.

4. Support is given to the conception of valence forces as highly localized and directive in character.

Princeton, New Jersey

---

[5] Vorländer, *Z. physik. Chem.*, **105**, 211 (1923).