radicals. Ogg and Williams[15] measured the competition between hydrogen iodide and iodine for methyl radicals in the gas phase. In contrast to the values above for liquid phase, iodine was found to be considerably more reactive than was hydrogen iodide. It is possible that the relative effectiveness of these radical scavengers was reversed by complexing of iodine with methyl iodide and cyclohexane[10] in the liquid phase.

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[15] R. A. Ogg, Jr., and R. R. Williams, Jr., THIS JOURNAL, **15**, 696 (1947).

[CONTRIBUTION FROM THE CHEMICALS RESEARCH DIVISION, ESSO RESEARCH AND ENGINEERING COMPANY]

The Dipole Moment of the Carbon–Carbon Bond

BY ANTHONY J. PETRO

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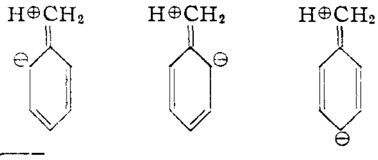
A simple vector model, based on the postulate that the covalent single bond between two differently hybridized carbon atoms is polarized, has been developed for predicting the dipole moments of certain molecules. Experimental evidence leading to this postulate is reviewed. Bond moments for the H–C bonds occurring in methane, ethylene and acetylene, taken from infrared dispersion measurements, have been used to calculate a limited number of bond moments involving the differently hybridized states of carbon. Omission of a non-zero bond moment for the $C(sp^3)$–$C(sp^2)$, $C(sp^2)$–$C(sp)$ and $C(sp^3)$–$C(sp)$ bonds has been shown to be inadequate for calculating molecular moments. Inclusion of the C–C moments in the vector model yields results in excellent agreement with observed values. The limits of applicability of this approach are given.

Introduction

The point of view that a molecular dipole moment is the vector sum of the various bond moments in a molecule has led to the successful elucidation of many molecular structures. In the development of this approach, bonds between atoms of the same element have been considered to have a zero moment. The purpose of this paper is to show that the dipole moments of certain molecules can be predicted simply and accurately by postulating a non-zero moment for the covalent single bond formed between two carbon atoms of different hybridization.

Hyperconjugation and Dipole Moments.—The symmetrical tetrahedral structure of methane, in which the four non-zero H–C bond moments are opposed, precludes a molecular dipole moment. Whereas substitution of one hydrogen atom in methane by a tetrahedral methyl group does not give rise to a dipolar molecule,[1] similar substitution by a phenyl group yields toluene which has a moment of 0.37 *D*.[2] Similar results are found in the cases of propene[2] and propyne,[3] for example. The geometry of the toluene molecule does not permit a resultant moment as long as all of the H–C bond moments are assumed equal. The theory of hyperconjugation[4] has, therefore, been resorted to in order to explain this apparently anomalous value. On this basis, the following polar structures have been written[5] for toluene each of the three forms being triply degenerate because of the indistinguishability of the three hydrogen atoms of the methyl group, there being nine such structures possible. The observed moment was then ascribed to very small contributions from each of these highly polar structures. Indeed, molecular orbital methods of calculation[6,7] have yielded moments in close agreement with the observed although, significantly, the two approaches have given quite different charge distributions in the toluene molecule.



The advent of nuclear magnetic resonance spectral analysis has served to shed new light on the problem. Since chemical shifts observed in proton resonances reflect differences in electron distribution about chemically non-equivalent protons, the n.m.r. spectrum of toluene should show splitting of the two proton lines corresponding to the ring and methyl group protons.

Corio and Dailey[8] determined the n.m.r. spectra of a number of monosubstituted benzenes and found the substances investigated to fall into two groups. One group consisted of those molecules which showed no splitting of the absorption line of the ring protons, *i.e.*, chemically equivalent protons. In this group were listed the substituents, CH_3, C_2H_5, Br, Cl, OH, OCH_3, CH_2Cl, $CHCl_2$, CN, CH_2OH and CH_2NH_2. In the second group were listed those substances which showed splitting of the ring proton absorption line and included the substituents NO_2, CHO, COCl, COOH, NH_2, I, and others. It must, therefore, be concluded that structures such as those pictured above (or a hybrid thereof) have no real existence when the substituent is one of those listed in the first group and that the explanation of the non-zero dipole moment of toluene must be sought elsewhere.

The Carbon–Hydrogen Bond Moment.—The magnitude and direction of the moment of the

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[1] C. P. Smyth and C. T. Zahn, THIS JOURNAL, **47**, 2501 (1925).

[2] K. B. McAlpine and C. P. Smyth, *ibid.*, **55**, 453 (1933).

[3] S. N. Ghosh, R. Trambarulo and W. Gordy, *Phys. Rev.*, **87**, 172 (1952).

[4] R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941).

[5] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, p. 315.

[6] B. Pullman and A. Pullman, "Les Théories électroniques de la chimie organique," Masson et Cie, Paris, 1952, Chapter VII.

[7] C. A. Coulson, "Valence," Oxford, London, 1952, Chapter XII.

[8] P. L. Corio and B. P. Dailey, THIS JOURNAL, **78**, 3043 (1956).

carbon–hydrogen bond has long been a matter of dispute.[9] In order to facilitate the formation of a table of bond moments, the H–C moment has been arbitrarily assigned a value of 0.4 *D* with direction $H^{+}{-}^{-}C$,[9] regardless of the hybridization of the carbon atom involved. That this is inaccurate can be seen easily when it is considered that the hydrogen atoms in methane are essentially chemically inert whereas in acetylene the hydrogen atoms are sufficiently acidic to be displaced by[10] elemental sodium, silver ion or cuprous ion. In addition, the bond energies and bond distances of the H–C bonds in methane, ethylene and acetylene are found to vary progressively.[11] Therefore, the H–C bonds in methane and acetylene are differently polarized, and since the carbon atoms are differently hybridized, it follows that the polarization of the H–C bond depends on the hybridized state of the carbon atom involved.

The value of the H–C bond moment has been determined by means of infrared dispersion measurements for each of the three hybridized states (sp^3, sp^2, sp) of carbon. Rollefson and Havens[12] obtained the value 0.307 *D* for the H–C (sp^3) bond in methane, Hammer[13] obtained the value 0.629 *D* for the H–C(sp^2) bond in ethylene and Kelly, *et al.*,[14] obtained the value 1.05 *D* for the H–C(sp) bond in acetylene. In each case the direction of the dipole was found to be $H^{+}{-}^{-}C$.

Similarly, it would be expected that the carbon-chlorine moment, for example, would be dependent on the hybridization of the carbon atom involved. Using the above H–C bond moments and assuming perfect tetrahedral, trigonal or digonal bonding, as the case may be, the values for the C–X moments, where X is F, Cl, Br, CN, also were calculated. The results are listed in Table I, under μ_B, together with the molecules and their observed dipole moments from which the bond moments were obtained. In the first column, the element listed to the right has the negative end of the dipole directed toward it.

The reason for the apparently smaller values of the aliphatic C(sp^2)–Cl and C(sp^2)–Br bond moments compared to those of the aromatic moments may be that, in the aliphatic molecule, the C–X and C–H bonds on the same carbon atom would reduce one another's moments by inductive effects much more than would the same moments on adjacent carbon atoms. Indeed, the difference, *ca.* 0.2 *D*, is of the same magnitude as the calculated inductive effect.[15] The values indicated for the aliphatic C(sp^2)–X bonds may, therefore, be considered effective values and still remain useful as long as internal consistency is maintained in the calculations.

Using the above H–C bond moment values, a simple vector calculation shows that, for toluene, the resultant of the H–C bond moments in the methyl group (0.31 *D*) and the opposing H–C bond moment at the *para* ring position (0.63 *D*) is 0.32 *D* as compared with the observed value of 0.37 *D*.[2]

TABLE I

CALCULATION OF BOND MOMENTS

H–C (sp^3) = 0.31 *D*
H–C (sp^2) = 0.63 *D*
H–C (sp) = 1.05 *D*

Bond	μ_B, *D*	μ_B calcd. from Molecule	μ, *D* obsd.
C(sp^3)–F	1.50	CH_3F	1.81[a]
C(sp^2)–F			
(aromatic)	0.95	C_6H_5F	1.58[b]
C(sp^3)–Cl	1.56	CH_3Cl	1.87[c]
C(sp^2)–Cl			
(aromatic)	1.07	C_6H_5Cl	1.70[d]
(aliphatic)	0.82	$CH_2{=}CHCl$	1.45[e]
Cl–C(sp)	0.61	$CH{\equiv}CCl$	0.44[f]
C(sp^3)–Br	1.49	CH_3Br	1.80[a]
C(sp^2)–Br			
(aromatic)	1.01	C_6H_5Br	1.64[g]
(aliphatic)	0.78	$CH_2{=}CHBr$	1.41[e]
C(sp^3)–CN	3.65	CH_3CN	3.96[h]
C(sp^2)–CN			
(aromatic)	3.51	C_6H_5CN	4.14[i]
(aliphatic)	3.57	$CH_2{=}CHCN$	3.88[j]
C(sp)–CN	2.55	$HC{\equiv}CCN$	3.60[k]

[a] C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.*, **2**, 499 (1934). [b] K. B. McAlpine and C. P. Smyth, *ibid.*, **3**, 55 (1935). [c] R. G. Shulman, B. P. Dailey and C. H. Townes, *Phys. Rev.*, **78**, 145 (1950). [d] L. G. Groves and S. Sugden, *J. Chem. Soc.*, 1094 (1934). [e] J. A. C. Hugill, I. E. Coop and L. E. Sutton, *Trans. Faraday Soc.*, **34**, 1518 (1938). [f] A. A. Westenberg, J. H. Goldstein and E. B. Wilson, Jr., *J. Chem. Phys.*, **17**, 1319 (1949). [g] R. J. W. LeFèvre and D. A. A. S. N. Rao, *Australian J. Chem.*, **8**, 140 (1955). [h] L. G. Groves and S. Sugden, *J. Chem. Soc.*, 158 (1937). [i] D. R. Lide, Jr., *J. Chem. Phys.*, **22**, 1577 (1954). [j] E. C. Hurdis and C. P. Smyth, THIS JOURNAL, **65**, 89 (1943). [k] A. A. Westenberg and E. B. Wilson, Jr., *ibid.*, **72**, 199 (1950).

Similar calculations were carried out on the molecules listed in Table II. The results which were obtained are listed under μ_I. As can be seen, the agreement between the calculated and observed values for the disubstituted compounds is rather poor compared to that which exists for the monosubstituted compounds. The simple approach used to obtain these results must, therefore, be considered inadequate.

Polarization of the Carbon–Carbon Bond.—It has been stated earlier that carbon–carbon bonds have been considered, heretofore, to be nonpolarized. However, if the polarization of the H–C bond depends on the hybridized state of the carbon atom, then a bond between two carbon atoms of different hybridization must be polarized. The magnitude of the bond moment would depend on the hybridization of each atom, there being three possibilities: C(sp^3)–C(sp^2), C(sp^3)–C(sp) and C(sp^2)–C(sp), which are found, for example, in toluene, propyne and phenylacetylene, respectively.

In order to calculate the values of these C–C moments the values for the H–C moments given in the preceding section were applied to the following

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(9) Ref. 5, pp. 240 ff.

(10) L. F. Fieser and M. Fieser, "Organic Chemistry," 3rd ed., Reinhold Publ. Corp., New York, N. Y., 1956, p. 91.

(11) H. Feilchenfeld, *J. Phys. Chem.*, **61**, 1133 (1957).

(12) R. Rollefson and R. Havens, *Phys. Rev.*, **57**, 710 (1940).

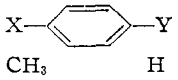
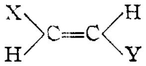
(13) C. F. Hammer, thesis, University of Wisconsin, 1948.

(14) R. L. Kelly, R. Rollefson and B. S. Schurin, *J. Chem. Phys.*, **19**, 1595 (1951).

(15) C. P. Smyth and K. B McAlpine, *ibid.*, **1**, 190 (1933).

TABLE II

CALCULATION OF MOLECULAR DIPOLE MOMENTS

Molecule X	Y	μ Obsd.	μ_1, D Calculated assuming zero C–C moments	μ_{II} Calcd. assuming non-zero C–C moments
				
CH_3	H	0.37[a]	0.32	*n*
$CH{\equiv}C$	H	0.73[b]	0.42	*n*
$CH{\equiv}C$	CH_3	1.01[c]	0.74	1.10
CH_3	F	2.00[d]	1.26	1.95
CH_3	Cl	1.94[e]	1.38	2.07
CH_3	Br	1.96[f]	1.46	2.01
CH_3	CN	4.37[g]	3.82	4.51
				
CH_3	H	0.35[a]	0.32	*n*
CH_3	Cl	1.97[h]	1.13	1.80
CH_3	Br	1.69[i]	1.09	1.76
CH_3	CN	4.50[j]	3.91	4.59
$X–C{\equiv}C–Y$				
CH_3	H	0.75[k]	0.74	*n*
C_4H_9	Cl	1.23[l]	0.30	1.18
C_4H_9	CN	4.21[m]	2.86	4.34

[a] See ref. 2. [b] H. Lumbroso, *Ann. fac. sci. univ. Toulouse sci. math. et sci. phys.*, 14, 108 (1950). [c] M. M. Otto and H. H. Wenzke, THIS JOURNAL, **56**, 1314 (1934). [d] E. M. Moore and M. E. Hobbs, *ibid.*, **71**, 411 (1949). [e] L. Tiganik, *Z. physik. Chem.*, **B13**, 425 (1931). [f] G. C. Hampson, R. H. Farmer and L. E. Sutton, *Proc. Roy. Soc.* (*London*), **A143**, 147 (1933). [g] H. Poltz, O. Steil and O. Stasser, *Z. physik. Chem.*, **B17**, 155 (1932). [h] N. B. Hannay and C. P. Smyth, THIS JOURNAL, **68**, 1005 (1946). [i] M. T. Rogers and M. B. Panish, *ibid.*, **77**, 4230 (1955). [j] See ref. *j*, Table I. [k] See ref. 3. [l] D. J. Pflaum and H. H. Wenzke, THIS JOURNAL, **56**, 1106 (1934). [m] B. C. Curran and H. H. Wenzke, *ibid.*, **59**, 943 (1937). [n] μ, obsd., used to calculate the corresponding C–C bond moment.

molecules to yield the indicated results

Toluene, $C^+(sp^3)–^-C(sp^2)$, $\mu = 0.69\ D$

Propylene, $C^+(sp^3)–^-C(sp^2)$, $\mu = 0.67\ D$

Phenylacetylene, $C^+(sp^2)–^-C(sp)$, $\mu = 1.15\ D$

Propyne $C^+(sp^3)–^-C(sp)$, $\mu = 1.48\ D$

These values, together with those listed in Table I, were then used to calculate the molecular dipole moments listed in Table II under μ_{II}. The calculated results are seen to be in rather good agreement with the observed, a decided improvement over the results listed under μ_I.

The attempt was made to test the present approach by calculating the moments of $C_6H_5CH{=}CHC{\equiv}CH$ (III) and $C_6H_5C{\equiv}CCH{=}CH_2$ (IV). The experimental values,[16] measured in benzene solution, were found to be $\mu_{III} = 0.97\ D$ and $\mu_{IV} = 0.24–0.27\ D$. Calculations predict the values to be $\mu_{III} = 0.73\ D$ and $\mu_{IV} = 0$. In calculating the experimental results, Lumbroso, *et al.*,[16] used the molar refractions for the D-sodium line, R_D, measured for the liquids, in place of the total induced polarization which is usually assumed to be[17] $1.03R_D$ to $1.15R_D$. In the case of IV, the induced polarization would have to be $1.026\ R_D$ in order to give the predicted zero moment. In the case of III, it would have to be $1.18R_D$, which is not so excessive that the calculated and observed values of the moment can be considered to be in poor agreement.

Conclusion

It has been shown that a simple vector model based on the postulate that the covalent single bond between two differently hybridized carbon atoms is polarized can be used, in some cases, to predict molecular dipole moments. The use of this approach, however, is limited to those molecules which contain substituent groups which (a) are sufficiently far apart to reduce mutual inductive effects to a minimum, and (b) do not strongly alter the electronic distribution in the remainder of the molecule by, *e.g.*, mesomeric effects. The calculations for the latter class of molecules must, unfortunately, be left to the much more complex methods of quantum mechanics.

It must be emphasized that the present approach is strictly empirical since an sp^3-hybridized carbon atom will be expected to change slightly with respect to its hybridization as its molecular surroundings are altered. As a result, some variations from the values calculated above must be expected, but within the stated limits of applicability the method can be employed successfully to calculate molecular moments.

Finally, the postulate presented in the preceding section can be quantitatively substantiated by analyses of appropriate infrared spectra since a permanently polarized bond requires an infrared-active stretching vibration. At the present time, the assignment[18] of the strong infrared absorption band at 919 cm.$^{-1}$ for the C–C stretching vibration in propylene appears to be the only such assignment made. It is possible that some of the absorption bands previously interpreted as harmonics of vibrations of other bonds may be, in reality, carbon–carbon stretching vibrations.

Acknowledgment.—The author wishes to express his gratitude to Professor Charles P. Smyth of Princeton University for his helpful suggestions and criticisms in the course of preparing this paper.

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(16) H. Lumbroso, R. Golse and A. Liermain, *Bull. soc. chim. France*, 1608 (1956).

(17) Ref. 5, p. 222.

(18) E. B. Wilson, Jr., and A. J. Wells, *J. Chem. Phys.*, **9**, 319 (1941).