THE DIPOLE MOMENTS OF THE DISUBSTITUTED BENZENES

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Recent measurements of the dipole moments of organic molecules[1] have shown that the symmetrical hydrocarbons have no electric moment and that their mono-derivatives possess moments varying with the nature of the substituent group. It has further been shown, in accordance with a prediction of J. J. Thomson,[2] that the moment of a disubstituted hydrocarbon may be calculated, in certain cases, from the assumption that it is the vector sum of individual moments characteristic of the substituent groups and that these group moments are directed along the conventional valence bonds joining the substituents to the hydrocarbon residue. Thus, for example, if it be supposed that the carbon atoms of the benzene nucleus are situated at the corners of a regular hexagon, the moment of a disubstituted benzene may be calculated from the law of cosines

$$M = \sqrt{m_1^2 + m_2^2 + 2\,m_1 m_2 \cos \beta} \qquad (1)$$

where M is the resultant moment of the molecule, m_1 and m_2 are the individual group moments, and β is the angle between m_1 and m_2. If the substituent groups are in the ortho position, $\beta = 60°$; if in the meta position, $\beta = 120°$; and if in the para position, $\beta = 180°$. It has been found that the groups —Cl, —Br, —I, —CH$_3$ and —NO$_2$ follow this rule approximately, but that the experimental data for compounds containing —OH, —NH$_2$ and —O— do not obey it even qualitatively. The discrepancies shown by the last named groups have been explained by the postulate that the resultant group moment does not lie along the valence bond of the usual structural formula. This seems quite probable since analysis of the infra-red spectra of H_2O and of NH_3 indicates a triangular model for the former and a pyramidal model for the latter. If this structure is preserved in the —OH and —NH$_2$ groups, it follows that these groups are unsymmetrical about the line joining the centers of the carbon and oxygen or carbon and nitrogen atoms. They may, therefore, be expected to exhibit a moment in some direction other than that of the line of centers. On the other hand, the groups which do follow the rule of vector additivity are symmetrical about the line of centers.

The moments calculated for those compounds which do obey the rule, however, show systematic variations from the experimental values. Thus

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[1] For reviews of this subject and references to the literature see C. P. Smyth. *Chem. Rev.*, **6**, 549 (1929); I. Estermann, *Ergebnisse Exak. Naturwiss.*, **8**, 258 (1929); H. Sack, *ibid.*, p. 307.

[2] J. J. Thomson, *Phil. Mag.*, **46**, 513 (1923).

the calculated moments of compounds of the type $o\text{-}C_6H_4X_2$ are from 10 to 30% higher than the experimental values. Höjendahl[3] has explained this by pointing out that the simple theory takes no account of interaction between the two dipoles. Such interaction might consist of either or both of two effects. In the first place there is a repulsive force between two dipoles in the ortho position which tends to force the dipoles apart, that is, to increase β of Equation 1. It is therefore possible to use β as an adjustable constant in order to bring the calculated value of M into agreement with the observed. In the second place, the dipoles may affect each other by induction. Since these molecules are not rigid and since each group is subjected to an electric force exerted by the other, dipole moments will be induced in each group in such a direction as to lessen the resultant moment. It is the purpose of the present paper to calculate the resultant moments of the disubstituted benzenes from the individual moments of the substituent groups, assuming that the group moments are directed along the valence bonds but taking into account the moments due to induction.

The dipole moment induced in any substituent as a result of an electric intensity $\mathbf{E}$ is given by the expression[4,5]

$$\mathbf{m}_i = \alpha \mathbf{E} \tag{2}$$

where α is the deformability of the substituent group. In the present case $\mathbf{E}$ is the force exerted by the dipole of the other constituent. If the dipole $\mathbf{m}$ exerting the force $\mathbf{E}$ is situated at the origin of a set of plane polar coördinates, the horizontal and vertical components of $\mathbf{E}(E_x$ and $E_y)$ at the point (r), are given by the equations.[6]

Equations 3 then follow since

$$E_x = -\frac{\partial\varphi}{\partial x} \text{ and } E_y = -\frac{\partial\varphi}{\partial y}$$

$$\left.\begin{array}{l} E_x = \dfrac{\xi}{r^3}(3\cos^2\vartheta - 1) + \dfrac{3\eta}{r^3}\sin\vartheta\cos\vartheta \\[2mm] E_y = \dfrac{3\xi}{r^3}\sin\vartheta\cos\vartheta + \dfrac{\eta}{r^3}(3\sin^2\vartheta - 1) \end{array}\right\} \tag{3}$$

where ξ and η are the horizontal and vertical components of $\mathbf{m}$.

In order to calculate the resultant moment, $\mathbf{M}$, of the molecule, it is

[3] K. Höjendahl, "Dissertation," Copenhagen, 1928; *Physik. Z.*, **30**, 391 (1929); *cf.* also Estermann, ref. 8.

[4] P. Debye, "Polar Molecules," The Chemical Catalog Co., Inc., New York, 1929.

[5] Throughout this article vector quantities will be indicated by bold face type.

[6] *Cf.* Jeans, "Electricity and Magnetism," Cambridge, 1925, p. 50. The potential, φ, at a point (x, y) due to charges $+ e$ at (a, b) and $-e$ at $(-a, -b)$ is

$$\varphi = \frac{e}{\{(x-a)^2 + (y-b)^2\}^{1/2}} - \frac{e}{\{(x+a)^2 + (y+b)^2\}^{1/2}}$$

Upon expanding this expression and neglecting squared and higher terms, it is found that

$$\varphi = \frac{2e(ax + by)}{(x^2 + y^2)^{3/2}} = \frac{\xi x + \eta y}{(x^2 + y^2)^{3/2}}$$

necessary to take into account the moments induced in the four un-substituted —CH groups. These moments may be represented by the symbol m_i'. M is then given by the expression

$$M = m_{o1} + m_{i1} + m_{o2} + m_{i2} + m_i' \qquad (4)$$

where m_{o1} and m_{o2} are the original moments of groups 1 and 2, m_{i1} and m_{i2} the corresponding induced moments and m_i' the resultant moment induced in the —CH groups.

In order to apply these equations it is necessary to know the dimensions of the molecules involved. Although x-ray diffraction data on crystals indicate a tilted model for the benzene nucleus,[7] chemical evidence together with the small electric moment of symmetrical tri-derivatives of benzene may be cited in favor of a plane model for the benzene ring in substituted compounds.[8] The question cannot be regarded as settled at present.
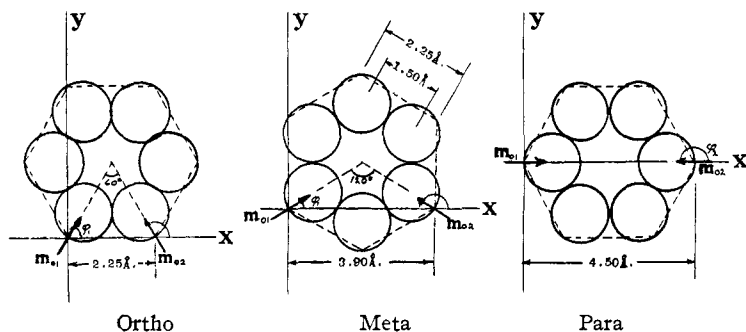

Ortho   Meta   Para

Fig. 1.—Benzene nuclei and positions of dipoles of substituent groups in ortho, meta and para compounds.

Since, however, the differences in the dimensions of the two models are too slight to affect the present calculations, the plane model has been chosen for the sake of simplicity. The radius of the carbon atom has been taken equal to 0.75 Å., the value obtained from crystal structure data. The centers of the six carbon atoms are therefore assumed to lie on the corners of a regular hexagon of side equal to 1.50 Å.

In order to locate the position of the dipoles associated with the substituent groups, they are assumed to be situated at the circumference of the carbon atoms to which the particular groups are attached, and to be directed along a diagonal of the hexagon. Thus in all the compounds the group moments are assumed to be situated at the corners of a regular hexagon of side equal to 2.25 Å. (Fig. 1). Using this model it follows that the distance between the dipoles of the two substituents is 2.25,

[7] W. H. Bragg and W. L. Bragg, "X-Rays and Crystal Structure," London, 1924, p. 229, ff.

[8] I. Estermann, *Leipziger Vorträge*, p. 34 (1929).

3.90 or 4.50 Å., according to whether the substituents are in the ortho, meta or para position.

It is next necessary to obtain numerical values for α. This quantity is related to the atomic refraction R by the equation

$$\alpha = 3R/4\pi N_A \qquad (5)$$

where N_A is the Avogadro number per mole. Since R varies with the wave length of the light used in its determination, the values must be extrapolated to infinite wave length. This has been done, using the assumption that the curve of R against λ becomes parallel to the λ axis in the region of the far infra-red. The values so obtained are tabulated in the first column of Table I. The quantity under consideration, however, is more a property of the bond between two atoms than of a single atom. It has, therefore, seemed advisable to use the octet refractions of the various groups in the calculations of α. The octet refraction was introduced by Smyth[9] and defined by him as

$$R_{oct} = R_{at} + \frac{1}{4}R_c \qquad (6)$$

Here R_{at} is the usual atomic refraction and R_c the atomic refraction of carbon. The values of R_{oct} are tabulated in the second column of Table I and those of α in the third column. This use of R_{oct} instead of R_{at} involves such a slight change in α that the final results are not appreciably affected.

TABLE I

Group	$R_{at}{}^a$	R_{oct}	$\alpha \times 10^{24}$	$m_c \times 10^{18}$		
—H	1.065	1.661[b]	0.654	0		
—Cl	5.789	6.38	2.51	−1.53[c]	−1.55[d]	−1.64[e]
—Br	8.636	9.23	3.63	−1.50[f]	−1.56[e]	
—I	13.297	13.89	5.46	−1.25[g]		
—CH₃	5.581	6.18	2.45	+0.43[e,f,h]		
—NO₂	6.39	6.99	2.75	−3.75[e]	−3.90[f]	

a Data from Landolt-Börnstein, "Physikalisch-Chemischen Tabellen," 5th ed., Berlin, 1923, p. 985, extrapolated to infinite wave length. *b* This is a "bond refraction" rather than an octet refraction. *c* C. P. Smyth, S. O. Morgan and J. C. Boyce, THIS JOURNAL, 50, 1536 (1928). *d* J. W. Williams and E. F. Ogg, *ibid.*, 50, 94 (1928). *e* K. Höjendahl, Ref. 3. *f* J. W. Williams, *Physik. Z.*, 29, 174, 204, 271, 683 (1928); THIS JOURNAL, 50, 2350 (1928). *g* P. Walden and O. Werner, *Z. physik. Chem.*, 2B, 10 (1929). *h* C. P. Smyth and S. O. Morgan, THIS JOURNAL, 49, 1030 (1927).

The experimental values of the moments of the monosubstituted compounds cannot be identified with the m_o's of Equation 4 since the former are the resultants of the latter and the moments induced in the five unsubstituted —CH groups. In order to calculate the actual group moment, $\mathbf{m_o}$, from the experimental value $\mathbf{m_e}$ consider a set of axes oriented with respect to the benzene ring as in Fig. 2. Since the molecule is symmetrical about the x-axis,

$$\Sigma \eta_i = 0$$

9 Smyth, *Phil. Mag.*, 50, 361 (1925); *cf.* also Fajans and Knorr, *Ber.*, 59, 249 (1926).

Then

$$m_e = m_o + \Sigma \xi_i$$
$$= m_o + 2\xi_{i2} + 2\xi_{i3} + \xi_{i4}$$

where ξ_{i2}, etc., are the x-components of the moments induced in the second —CH group and so on. Substituting from Equations 3 it follows that

$$m_e = 1.013 m_o \tag{7}$$

if it be assumed that the fields of the induced moments are too small to produce an appreciable effect upon m_o.

The foregoing assumption is valid only because the induced moments are small as a result of the small deformability of the —CH group. In calculating the moments induced in the substituent groups themselves, in the case of the disubstituted compounds, it is necessary to take into account the fields of the induced moments as well as those of the original moments. This can be done by substituting in the equations

$$\xi = \xi_o + \xi_i \tag{8}$$
$$\eta = \eta_o + \eta_i$$

Fig. 2.

where ξ_o, η_o are the components of the original group moment and ξ_i, η_i the components of the moment induced in that group by the second dipole.

Finally, it is necessary to calculate m_i', the moments induced in the unsubstituted —CH groups. This calculation is quite analogous to that leading to Equation 7. In this case, however, as well as in the final calculation, it is advantageous to choose the coördinate axes so that the substituent groups both lie on the x-axis (Fig. 1). Assuming, as before, that the moments induced in the —CH groups are too small to affect each other or the inducing groups, the total components of the former are found to be

$$\xi_i' = A'(\xi_1 + \xi_2) + A''(\eta_1 - \eta_2)$$
$$\eta_i' = B'(\xi_1 - \xi_2) + B''(\eta_1 + \eta_2) \tag{9}$$

Here the subscripts 1,2 refer to groups 1,2. The ξ, η are the components of the total moments of the substituent groups. The A's and B's are numerical coefficients depending on the deformability of the —CH group and on the dimensions of the molecule. Their values are

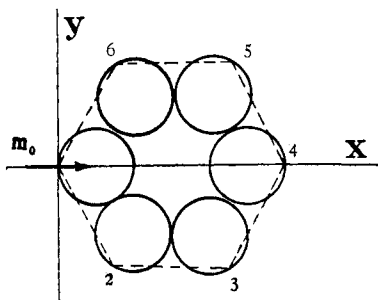|	Ortho	Meta	Para
A'	-0.01339	$+0.0206$	$+0.001083$
A''	$-.0511$	$-.0511$	0
B'	$-.0511$	$-.0511$	0
B''	$+.1001$	$+.1125$	0

The resultant moment of the molecule may now be obtained by substituting Equations 2, 3, 8 and 9 in Equation 4. The result is

$$M^2 = \left[(1 + A') \left(\frac{(1 + 2a_2)\xi_{o1} + (1 + 2a_1)\xi_{o2}}{1 - 4a_1a_2} \right) + A'' \left(\frac{(1 + a_2)\eta_{o1} - (1 + a_1)\eta_{o2}}{1 - a_1a_2} \right) \right]^2 +$$
$$\left[(1 + B'') \left(\frac{(1 - a_2)\eta_{o1} + (1 - a_1)\eta_{o2}}{1 - a_1a_2} \right) + B' \left(\frac{(1 - 2a_2)\xi_{o1} - (1 - 2a_1)\xi_{o2}}{1 - 4a_1a_2} \right) \right]^2 \quad (10)$$

where a_1 and a_2 are equal to α_1/r^3 and α_2/r^3, respectively. ξ_{o1} and η_{o1} are obtained from Fig. 1 and Equation 7.

$$\xi_{o1} = \frac{\cos \varphi_1}{1.013} m_{e1} \qquad \eta_{o1} = \frac{\sin \varphi_1}{1.013} m_{e1} \quad (11)$$

Similar equations give ξ_{o2} and η_{o2}. It should be noted that Equation 10 contains no adjustable constants.

Upon selecting values of m_e with which to test Equation 10 it becomes apparent that the accuracy of the data given in the literature leaves much to be desired. Since the experimental data vary with the method and apparatus used, the relative agreement is better than the absolute. It has therefore seemed advisable, wherever possible, to use in the calculation of M that value of m_e determined by the same experimenter who measured M. Although in general better than the absolute, the relative agreement is not good in all cases. For example, the values obtained by Williams and by Höjendahl for the moment of o-dinitrobenzene, 6.05 × 10⁻¹⁸ and 6.00 × 10⁻¹⁸, respectively, are in good agreement, but their results for nitrobenzene, 3.90 × 10⁻¹⁸ and 3.75 × 10⁻¹⁸ show greater divergence.

The values of m_e used in the calculation are tabulated in the last column of Table I. The plus and minus signs indicate that some of the dipoles point toward and others away from the center of the ring. The assignment of sign to any one group is quite arbitrary. Once it is fixed, however, the signs of the other groups are definitely established.

The results of the calculations are summarized in Table II. Here the names of the compounds are given in the first column, the experimental

TABLE II

DIPOLE MOMENTS × 10¹⁸

Compound	M, obs.	M, calcd., approx.	Δ_1	M, calcd., Eq. 10	Δ_2	M'	Δ_3	Remarks
o-$C_6H_4Cl_2$	2.25[a]	2.68	−0.33	2.30	−0.05	2.16	+0.09	$m_e = 1.53$
m-$C_6H_4Cl_2$	1.48[a]	1.55	− .07	1.48	0	1.44	+ .04	$m_e = 1.53$
p-$C_6H_4Cl_2$	0[a]	0		0		0		
o-$C_6H_4Br_2$	1.87[b]	2.60	− .73	2.09	− .22	1.94	− .05	$m_e = 1.50$
m-$C_6H_4Br_2$	1.55[b]	1.50	+ .05	1.43	+ .12	1.37	+ .18	$m_e = 1.50$
p-$C_6H_4Br_2$	0[b]	0		0		0		
o-$C_6H_4I_2$	1.63[c]	2.17	− .54	1.56	+ .07	1.43	+ .20	$m_e = 1.25$
m-$C_6H_4I_2$	1.01[c]	1.25	− .24	1.14	− .13	1.10	− .09	$m_e = 1.25$
p-$C_6H_4I_2$	..	0		0		0		

TABLE II (*Concluded*)

Compound	M, obs.	M calcd., approx.	Δ_1	M calcd., Eq. 10	Δ_2	M'	Δ_3	Remarks
o-$C_6H_4(CH_3)_2$	0.58^d	0.75	-0.17	0.65	-0.07	0.61	-0.03	$m_e = 0.43$
m-$C_6H_4(CH_3)_2$	0.46^e	0.43	$+ .03$	0.42	$+ .04$	0.41	$+ .05$	$m_e = 0.43$
p-$C_6H_4(CH_3)_2$	0^d	0		0		0		
o-$C_6H_4(NO_2)_2$	6.05^d	6.75	$- .70$	5.80	$+ .25$	5.39	$+ .66$	$m_e = 3.90$
m-$C_6H_4(NO_2)_2$	3.81^d	3.90	$- .09$	3.77	$+ .04$	3.68	$+ .13$	$m_e = 3.90$
p-$C_6H_4(NO_2)_2$	0^d	0		0		0		
p-C_6H_4ClBr	0.1^d	0.05	$+ .05$	0.09	$+ .01$	0.09	$+ .01$	$m_{e1} = 1.55$
								$m_{e2} = 1.50$
o-C_6H_4BrI	1.73^b	2.38	$- .65$	2.09	$- .36$	1.78	$- .05$	$m_{e1} = 1.50$
								$m_{e2} = 1.25$
m-C_6H_4BrI	1.14^b	1.39	$- .25$	1.34	$- .20$	1.32	$- .18$	$m_{e1} = 1.50$
								$m_{e2} = 1.25$
p-C_6H_4BrI	0.49^b	0.25	$+ .24$	0.33	$+ .16$	0.33	$+ .16$	$m_{e1} = 1.50$
								$m_{e2} = 1.25$
o-$C_6H_4ClNO_2$	4.25^f	4.78	$- .53$	4.39	$- .14$	4.16	$+ .09$	$m_{e1} = 1.64$
								$m_{e2} = 3.75$
m-$C_6H_4ClNO_2$	3.38^f	3.26	$+ .12$	3.30	$+ .08$	3.28	$+ .10$	$m_{e1} = 1.64$
								$m_{e2} = 3.75$
p-$C_6H_4ClNO_2$	2.55^f	2.11	$+ .44$	2.21	$+ .34$	2.21	$+ .34$	$m_{e1} = 1.64$
								$m_{e2} = 3.75$
p-$C_6H_4BrNO_2$	2.53^f	2.19	$+ .34$	2.37	$+ .16$	2.37	$+ .16$	$m_{e1} = 1.56$
								$m_{e2} = 3.75$
o-$C_6H_4CH_3Cl$	1.39^b	1.38	$+ .01$	1.81	$- .42$	1.65	$- .26$	$m_{e1} = 0.43$
								$m_{e2} = 1.55$
m-$C_6H_4CH_3Cl$	1.60^b	1.81	$- .21$	1.91	$- .31$	1.93	$- .33$	$m_{e1} = 0.43$
								$m_{e2} = 1.55$
p-$C_6H_4CH_3Cl$	1.74^b	1.98	$- .24$	2.06	$- .32$	2.06	$- .32$	$m_{e1} = 0.43$
								$m_{e2} = 1.55$
o-$C_6H_4CH_3NO_2$	3.75^d	3.70	$+ .05$	4.45	$- .70$	3.98	$- .23$	$m_{e1} = 0.43$
								$m_{e2} = 3.90$
m-$C_6H_4CH_3NO_2$	4.20^d	4.13	$+ .07$	4.35	$- .15$	4.23	$- .03$	$m_{e1} = 0.43$
								$m_{e2} = 3.90$
p-$C_6H_4CH_3NO_2$	4.5^d	4.33	$+ .17$	4.51	$- .01$	4.51	$- .01$	$m_{e1} = 0.43$
								$m_{e2} = 3.90$

[a] Smyth, Morgan and Boyce, *loc. cit.* [b] Walden and Werner, *loc. cit.* [c] J. Errera, "Polarisation Dielectrique," Paris, 1928. [d] Williams, *loc. cit.* [e] Smyth and Morgan, *loc. cit.* [f] Höjendahl, *loc. cit.*

values of M in the second and, in the third, the values of M calculated from the approximate equation (1). In the fourth column are listed the differences between the observed values of M and the approximate calculated values (Δ_1). The values of M calculated from Equation 10 are given in the fifth column. In the sixth are listed the differences between the observed values and those calculated taking into account the

effect of induction (Δ_2). The figures listed under the headings M' and Δ_3 will be discussed below. In the last column, headed "Remarks," are tabulated the values of m_e used in the calculations.

Inspection of Table II shows that all the values calculated from the assumption of interaction by induction, except for two groups of compounds, are nearer to the observed values than are those calculated from the approximate equation (1). For most compounds the agreement is within the experimental error. The cases in which the agreement is not good will be referred to later.

The Referee to whom this paper was referred, in order to pass upon its suitability for publication, criticized the method of calculation on the grounds that changes in the moments of the —C—C— bonds of the benzene nucleus should have been taken into account, since the changes in the —CH bonds are considered. We wish to express our indebtedness to him for raising this point. The omission was due to the fact that the effect of the —CH bonds is altered by the entrance of the second substituent group since in the disubstituted compound there is one less —CH bond than in the monosubstituted. The number of —C—C— bonds is the same in both types of compounds. Hence it seemed permissible to neglect the latter. For the sake of completeness, however, the calculations have been repeated taking into account the changes in the moments of the —C—C— bonds. This extension of the calculation merely involves using different values for the proportionality constant of Equation 7 and for the constants A', A'', B' and B'' of Equations 9. To arrive at numerical values for these constants it was assumed that the induced moments in question are located at the "points of contact" of the carbon atoms. α_{cc} was taken equal to 0.984×10^{-24} since

$$R_{cc} = \frac{1}{6}(R_{C_6H_6} - 6R_{CH})$$

The constant of Equation 7 then turns out to be 2.38 instead of 1.013 and the others are

	Ortho	Meta	Para
A'	0.1159	0.939	1.348
A''	.712	.712	0
B'	.712	.712	0
B''	.939	.1159	0

The results obtained with the use of these values are listed in Table II under the headings M' and Δ_3. In most cases the values of M' do not differ essentially from those for $M_{calcd.}$ previously obtained, as is to be expected. In general the agreement between calculated and observed is slightly better than before. The improvement is greatest for the chlorotoluenes and o-nitrotoluene, but for these compounds the agreement still is not as good as might be desired. Moreover, consideration of the —C—C—

bonds makes the agreement in the cases of o-dinitrobenzene definitely worse. It is difficult to explain these discrepancies. The inconsistency of the experimental data for nitrobenzene has already been pointed out. Perhaps in the chlorotoluenes and o-nitrotoluene there is some other type of interaction between the substituent groups. It is unfortunate that there are available no other measurements upon compounds of this type, namely, compounds in which one dipole is directed toward and the other away from the center of the ring.

One further point must be considered in connection with calculations of this type. This is that, under sufficiently great electric intensity, Equation 2 is no longer valid since α must eventually decrease as E increases. The reality of this effect may be observed in Debye's[10] calculation of the moment of HCl. Furthermore, we have attempted to apply the methods of this paper to the derivatives of methane. In this case the correction term is again much too large, indicating that the region of validity of Equation 2 has been exceeded. Apparently the present methods cannot be employed when the distance from the inducing dipole is much less than 2 Å. On taking into account the —C—C— bonds in the above calculations, however, it is necessary to consider distances considerably smaller than this. That the results are satisfactory is only due to the fact, previously pointed out, that the effect of the —C—C— bonds very nearly cancels out of the resultant moment.

The determining factor in the correction for induction is the distance between the dipoles, since this enters to the third power. The results show that a correction of this type leads to concordant results only when the dipoles are assumed to be situated at the circumference of the carbon atoms. If the dipoles are assumed to be at the center of the substituent group, the effect considered in this paper is negligible. If they are assumed to be at the centers of the carbon atoms, this correction is far too large.

Summary

The calculated dipole moments of the disubstituted benzenes have been corrected for the effect of the mutual induction of the dipoles. The results show. that, in order that a correction of this kind be successful, the dipoles must be assumed to be located on the circumferences of the carbon atoms, that is, at the conventional valence bond.

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[10] P. Debye, Ref. 4. p 62.