to the top of the tube. Small amounts of hydrogen are formed at the same time.

Density of $BCl_3 \cdot PH_3$ in the Gas Phase.—40.3 cc. of $BCl_3 \cdot PH_3$ weighs 0.1230 g. The calculated weight of this volume of gas, if complete dissociation is assumed, and the product acted as a perfect gas, would be 0.1340 g.

Decomposition Pressure of $BCl_3 \cdot PH_3$.—The pressure of $BCl_3 \cdot PH_3$ was determined between −11 and +25°, the results being expressed by the equation $\log p = 11.137 - 2810/T$. The maximum deviation of the observed from the calculated pressures does not exceed 0.5 mm.

Reaction of Hydrogen Bromide on Diborane Diphosphine.—Hydrogen bromide reacts in much the same way as hydrogen chloride, the reaction of liquid hydrogen bromide at −78° taking place very rapidly.

Summary

1. Diborane and phosphine react to form a white unstable solid. The reaction takes place in the gas phase above −30° and in the liquid phase above −110°. The properties of the substance were studied and its probable structure discussed.

2. The action of ammonia on diborane diphosphine has been investigated over a temperature range of −75 to +25°. Liquid ammonia has been found to displace from 52 to 58% and gaseous ammonia up to 75% of the phosphine in diborane diphosphine.

3. The action of hydrogen chloride and hydrogen bromide on diborane diphosphine was found to result in the splitting out of hydrogen attached to boron. The compounds $B_2H_4Cl_2 \cdot 2PH_3$, $B_2H_2Cl_4 \cdot 2PH_3$ and $BCl_3 \cdot PH_3$ have been obtained by this reaction.

4. Attempts to prepare a volatile compound $B_3P_3H_6$, the analog of the cyclic compound $B_3N_3H_6$, were unsuccessful.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dipole Moment, Induction and Resonance in Tetra-, Penta- and Hexa-substituted Benzenes

BY CHARLES P. SMYTH AND GEORGE L. LEWIS

The dipole moments of a great many poly-substituted benzenes have been measured by numerous investigators, but the loan by Dr. S. O. Morgan of the Bell Telephone Laboratories of fourteen such compounds, only one of which had been previously measured, has given us an unusual opportunity for the study of a large number of closely related compounds obtained from a single source. In the cases of most of the poly-substituted benzenes, departures of the moments from the values calculated as the resultants of the moments produced by the individual substituents have been attributed to mutual repulsion between adjacent atoms, which has since been shown by X-ray and electron diffraction to produce little distortion in most cases, and to mutual induction between adjacent groups, which calculation has shown to be sufficient to account for the observed discrepancies. More recently, the development of our ideas of resonance has brought the explanation not only of differences in moment between mono-substituted aromatic and aliphatic hydrocarbons, but also of a few seeming discrepancies in the moments of poly-substituted benzenes not previously accounted for. Although Groves and Sugden[1] have refined the method of calculating the inductive effect of a dipole upon the various atoms of the molecule containing it, the calculation retains the fundamental uncertainty inherent in the treatment of a distribution of charges as a single dipole located at a point and in the decision as to the proper location of this point. This uncertainty is serious only in calculating the inductive effects of the dipole upon the immediately adjacent atoms, but it is just these effects which make up the major part of the inductive shifts produced by the dipole. Although reasonable and, at times, very satisfactory results have been obtained on the basis of plausible assumptions in both the more and the less refined calculations, the inductive effect will be treated here in an empirical manner, rendered convenient by the number of but slightly differing compounds under examination.

Consideration of the moments obtained in the present work, like that of nearly all poly-substituted benzenes previously treated, loses a certain amount of precision because of the solvent effect, as the low volatility of the substances has

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

necessitated their measurement in benzene solution. However, as the dipoles in the fourteen molecules considered here lie in the plane of the benzene ring and as the maximum polarizabilities of the molecules, with a slight deviation in the case of pentachloroethylbenzene, must also lie in this plane and should not vary a great deal with the direction in this plane, the moments observed in benzene solution should be somewhat lower than the gas values,[2] but the small lowering should be relatively much the same for the different molecules, which should, therefore, have rather closely comparable moment values. The difference in solvent effect between these poly-substituted benzenes and those of mono-substituted benzenes should probably be greater than the differences among the solvent effects of the poly-substituted benzenes. However, the moments of mono- and disubstituted benzenes measured in solution will be used in discussing those of the tetra-, penta-, and hexa-substituted molecules. In general accord with what has been said in regard to the lowering of the moment by solvent effect in the more highly substituted benzenes, it may be mentioned that the moments found by Groves and Sugden[3] for the following vapors are higher than those listed by Fuchs and Wolf[4] for the substances in solution by the amount ($\times 10^{18}$) given after each: m-$C_6H_4Cl_2$, 0.19; o-$ClC_6H_4NO_2$, 0.29; m-$ClC_6H_4NO_2$, 0.30; p-$ClC_6H_4NO_2$, 0.23. The value reported by Groves and Sugden for o-$C_6H_4Cl_2$ vapor is 0.11 lower than the often-measured solution value, 2.27, while, on the basis of the theoretical considerations qualitatively applied and the experimental values just cited as well as the 0.15 lower value of monochlorobenzene in solution, 1.55, than in the vapor, the vapor value might be expected to be higher than that in solution. This single seeming discrepancy does not invalidate our method of approach, but does show the element of uncertainty involved in the comparison of values from different sources.

The solution values of the mono-substituted benzenes, 1.55 for chlorobenzene and 4.00 for nitrobenzene, to be used in the discussion are 0.15 and 0.21 lower than the gas values. The average moment value 0.34 calculated for toluene from the differences between the molar refraction for the D sodium line and the polarizations measured[5] for the pure liquid from -90 to $+90°$ is indistinguishable from the vapor value 0.35 obtained from the variation of polarization with temperature.[6] If, however, the moment is calculated for the vapor from the differences between the molar refraction and the polarization, a constant value 0.45 is obtained, which, probably, represents the upper limit assignable to the toluene moment. The value 0.35 will be used in the calculations of the present paper.

Experimental Data

As previously indicated, the substituted benzenes were obtained through the kindness of Dr. S. O. Morgan of the Bell Telephone Laboratories and were used without further purification. The benzene used as solvent was purified in the usual manner.[7] The dielectric constants of the solutions were measured at a frequency of 520 kilocycles with a crystal-controlled heterodyne beat apparatus described elsewhere[5] and the densities were measured with an Ostwald–Sprengel pycnometer in the manner previously described.[8] The dielectric constants ϵ and densities d of the solutions containing mole fractions c_2 of solute are given in Table I together with the polarizations P_2 calculated from them and the value P_1 for the solvent. The value of P_∞ for each substance at 25° given in Table II was obtained by extrapolation of the P_2 values to infinite dilution. The dipole moment μ was calculated in the usual manner from the difference between P_∞ and the molar refraction MR_D listed in Table II. As the substances were solid at room temperature, the molar refractions were calculated as additive quantities from the refraction data in "Landolt–Börnstein." The accuracy of these calculated values is equal to that obtainable experimentally in moderately dilute solutions and greater than that obtainable in the most concentrated solutions that could be prepared from the least soluble substances under examination. The smallness of the differences found between P_∞ and MR_D for the symmetrical trichloromesitylene and dichlorodurene give evidence of the accuracy of the MR_D values. The two small moment values calculated from these differences and listed in parentheses are, of course, indistinguishable from zero and indicate zero moments just as do similar small values obtained for liquid carbon tetrachloride and benzene. The somewhat larger moment values of 2,4,6-trichlorotoluene and pentachlorobenzene have probable errors of about 15% and 5%, respectively, because of uncertainty as to atomic polarization, and the remaining values, all higher, have probable errors of about 1%, with the exception of that for the difficultly soluble pentachlorotoluene, which has a probable error of about 5%. In Table II all the substances are named as substituted benzenes, the order of listing being the same as in Table I.

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[2] See Higasi, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **28**, 284 (1936).

[3] Groves and Sugden, *J. Chem. Soc.*, 1782 (1937).

[4] Fuchs and Wolf, "Hand- und Jahrbuch der chemischen Physik," Vol. VI, Akademische Verlagsgesellschaft m. b. H., Leipzig, 1935, Appendix.

[5] Lewis and Smyth, *J. Chem. Phys.*, **7**, 1085 (1939).

[6] McAlpine and Smyth, THIS JOURNAL, **55**, 453 (1933).

[7] Smyth and Walls, *ibid.*, **54**, 1854 (1932).

[8] Lewis and Smyth, *ibid.*, **61**, 3063 (1939).

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS IN BENZENE AND POLARIZATIONS AT 25°

c_2	ϵ	d	P_2
Pentamethylchlorobenzene			
0.00000	2.2760	0.87321	(26.672 = P_1)
.01099	2.3310	.87710	124.7
.02077	2.3788	.88062	123.5
.03315	2.4374	.88460	122.5
.03998	2.4690	.88688	121.8
.04448	2.4997	.88861	124.3
.04612	2.490	.88892	121.8
Pentachlorotoluene			
.00354	2.2909	.87823	107.9
.00504	2.2965	.88027	106.1
.00682	2.3027	.88265	104.4
.00856	2.3082	.88490	102.7
.00892	2.3093	.88536	102.5
Pentachloroethylbenzene			
.01440	2.3286	.89296	106.3
.02594	2.3704	.90797	106.6
.02875	2.3807	.91172	106.6
.03657	2.4081	.92239	105.8
.04313	2.4338	.93092	106.4
Pentachlorobenzene			
.00941	2.2893	.88614	64.1
.02469	2.3139	.90618	66.8
.03108	2.3237	.91451	66.8
.04635	2.3472	.93442	66.8
.05737	2.3642	.94854	66.8
1,2,3,4-Tetrachlorobenzene			
.01521	2.3530	.88931	115.0
.02383	2.3892	.89831	110.1
.03033	2.4185	.90516	108.9
.04014	2.4550	.91531	105.2
Trichloromesitylene			
.00544	2.2776	.87781	56.6
.00753	2.2780	.87957	55.6
.01040	2.2790	.88200	55.5
Dichlorodurene			
.00632	2.2789	.87700	57.8
.00887	2.2796	.87861	56.7
.01344	2.2819	.88131	57.2
.01762	2.2833	.88385	56.8
.02133	2.2848	.88605	56.7
.02766	2.2876	.89033	56.3
2,4,6-Trichlorotoluene			
.04429	2.3063	.90357	51.4
.09227	2.3397	.93642	51.2
.15289	2.3803	.97781	50.7
.21281	2.4218	1.01889	50.3
Trichloropseudocumene			
.00636	2.3078	0.87874	122.9
.00779	2.3157	.87994	124.4
.01019	2.3279	.88193	124.4
.01177	2.3359	.88321	124.4
.01392	2.3468	.88493	124.6
Tetrachloro-*o*-xylene			
.00163	2.2932	.87502	204
.00232	2.2998	.87579	199
.00304	2.3072	.87658	199
.00394	2.3171	.87754	202
.00478	2.3238	.87850	195
4,5-Dichloro-*o*-xylene			
.01806	2.5062	.88298	222.4
.03660	2.7291	.89250	211.2
.05009	2.8875	.89943	204.9
.06201	3.0220	.90546	199.3
.07487	3.1641	.91187	194.1
3,4,5-Trichloro-*o*-xylene			
.00613	2.3285	.87807	172.5
.01228	2.3803	.88293	170.2
.01453	2.3976	.88421	169.2
.02369	2.4640	.89089	162.1
Dichloroprehnitene			
.00213	2.3028	.87458	233
.00403	2.3264	.87577	233
.00564	2.3471	.87673	233
.00802	2.3770	.87814	232.2
.00976	2.3990	.87912	231.8
Dinitroprehnitene			
.00201	2.4110	.87480	1009
.00460	2.5857	.87684	977
.00715	2.7584	.87891	947
.01003	2.9571	.88126	914
.01425	3.2416	.88450	873.4
.01941	3.6013	.88857	830.4

TABLE II

MOLAR REFRACTIONS (CALCULATED), POLARIZATIONS (25°), AND MOMENTS

	MR_D	P_∞ (25°)	μ ($\times 10^{18}$)
Pentamethylchlorobenzene	55.0	126.0	1.85
Pentachloromethylbenzene	55.4	105	1.55
Pentachloroethylbenzene	60.1	106.6	1.50
Pentachlorobenzene	50.6	66.8	0.88
1,2,3,4-Tetrachlorobenzene	45.8	120.8	1.90
1,3,5-Trimethyl-2,4,6-trichlorobenzene	55.3	55.8	(0.1)
1,2,4,5-Tetramethyl-3,6-dichlorobenzene	55.6	56.9	(.25)
2,4,6-Trichloromethylbenzene	45.6	51.6	.54
1,2,5-Trimethyl-3,4,6-trichlorobenzene	55.3	124.4	1.83
Tetrachloro-*o*-xylene	55.2	201	2.65
1,2-Dimethyl-4,5-dichlorobenzene	45.8	233	3.01
1,2-Dimethyl-3,4,5-trichlorobenzene	50.4	176	2.46
1,2,3,4-Tetramethyl-5,6-dichlorobenzene	55.0	233	2.93
1,2,3,4-Tetramethyl-5,6-dinitrobenzene	58.2	1035	6.86

Discussion of Results

In discussing the dipole moments in Table II, we are primarily concerned with the effects of the methyl, chloro, and nitro groups upon one another and upon the benzene ring to which they are attached. Unless otherwise indicated, the moment values quoted are taken from the summary of Fuchs and Wolf already referred to.[4]

It is well known that the methyl group is classed with the halogens in its orienting effect upon substitution in the benzene ring. The small moment of toluene has been attributed by some investigators to the C–H bond moments of the methyl group, it being assumed tacitly and without reason that the aromatic C–H bond moment is zero. The orienting effect of the methyl group shows that it produces some alteration in the distribution of charge in the ring, which should contribute to the moment. That this moment contribution acts in the direction of the C–C bond between the ring and the methyl group, as would be expected, is shown by the fact that the allocation of the entire dipole moment to this axis leads to good agreement between the calculated and the observed moments when additional groups are substituted on the ring. The small moment of the para aromatic H–C bond is included in the value used for each monosubstituted benzene moment and cancels out when these moments are added and subtracted. The fact that the length of the C–C bond between the ring and the methyl group in mesitylene and hexamethylbenzene cannot be distinguished from that of an ordinary aliphatic C–C bond,[9] is consistent with the absence of any very profound disturbance of structure as shown by the smallness of the dipole moment.

The moment values 0.5 and 0.4 determined in solution for *o*- and *m*-xylene respectively differ by no more than the probable errors in their measurement from the values 0.61 and 0.35 calculated by assigning a moment 0.35 to each axis of the ring-to-methyl bonds. The observed moment of *p*-chlorotoluene 1.90 is identical with the value calculated as the sum of the toluene moment 0.35 and the chlorobenzene moment 1.55, the observed value 1.78 for *m*-chlorotoluene agrees well with the resultant 1.75 of the two vectors 0.35 and 1.55, with an angle 120° between them, and the moment of the ortho compound 1.35 is but slightly lower than the value 1.41 calculated with an angle 60° between the two vectors. The agreement between the observed and calculated values of the three bromotoluenes is equally good.

While the *p*- and *m*-dichlorobenzene moments agree well with the calculated values the moment of the ortho compound determined in solution is 15% lower than the resultant of two dipoles of moment 1.55 with an angle 60° between them. This lowering must be attributed to mutual induction since the widening of the angle between the dipoles because of mutual repulsion has been shown by electron diffraction measurements[10] to be only of the order of 1°. It is well known that the moment of monochlorobenzene is lowered through resonance with contributions from structures in which a positively charged chlorine is connected to the ring by a double bond and a negative charge occurs on the para or on one of the two ortho carbons. It would be expected that substitution of additional chlorines on the ring would lessen the occurrence of the double bond between any particular chlorine and the ring and thus increase the dipole moment associated with the bond. The shortening of the carbon–chlorine bond by its partial double bond character has been observed by means of electron diffraction,[10] but the possible variation in this shortening with variation in the degree of double bond character which might be expected to accompany variation in the number of chlorines was not apparent here as it was in the case of the chloroethylenes.[11] The fair agreement between the observed and calculated values of *m*-dichlorobenzene, in which the effect of mutual induction is small shows that any increase of moment caused by decrease in double bond character must be small.

The agreement between the observed and calculated values of the chlorotoluenes and the fact that chloromesitylene has the same moment 1.55 as chlorobenzene while bromomesitylene and bromodurene[12] have moments 1.52 and 1.55, respectively, as compared to 1.52 for bromobenzene, show that the effects of the methyl groups upon the structures contributing to that of chlorobenzene as well as the inductive effect between the halogen and the adjacent methyl are too small to be detected in the moments.

This absence of effect of the methylbenzene upon the chlorobenzene moment is further evidenced by the moments in Table II. In pentamethylchlorobenzene, the moments due to the 2,3-methyl groups should cancel those due to the 5,6-methyl groups, leaving a moment equal to that of *p*-chlorotoluene. The observed value 1.85 is in satisfactory agreement with the observed value of *p*-chlorotoluene 1.90, which has been found identical with the calculated value. Similar treatment of pentachlorotoluene and penta-

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[9] Pauling and Brockway, THIS JOURNAL, **59**, 1223 (1937).

[10] Brockway and Palmer, *ibid.*, **59**, 2181 (1937).

[11] Brockway, Beach and Pauling, *ibid.*, **57**, 2693, 2705 (1935).

[12] Birtles and Hampson, *J. Chem. Soc.*, 10 (1937).

chloroethylbenzene would have the moments due to the 2,3-chlorines cancelling those due to the 5,6-chlorines leaving moments equal to those of *p*-chlorotoluene and *p*-chloroethylbenzene, which should be almost identical in value. The observed values 1.55 and 1.50 are considerably lower than that of *p*-chlorotoluene because of induction between the chlorines. Indeed, it is surprising that they are not still lower. This will be clearer after consideration of the moments of tri-, tetra- and pentachlorobenzenes. The previously determined moment of 1,2,4-trichlorobenzene is 1.25. In the absence of inductive effects, the moments due to the 1,4-chlorines should cancel each other leaving a moment equal to that of chlorobenzene 1.55, but the moment of *o*-dichlorobenzene 2.27, 15% lower than the calculated value, has given evidence of strong mutual induction. If the resultant of the 1,2-chlorine moments is taken equal to that of *o*-dichlorobenzene and acting in the line bisecting a 60° angle between the bonds of the 1,2-chlorines, and the usual moment 1.55 is assigned to the 4-chlorine, the resultant moment of the molecule is calculated to be 1.21 in excellent agreement with the observed value 1.25. In 1,2,3,5-tetrachlorobenzene, the 2- and the 5-chlorine moments should, in the absence of induction, cancel one another, while the 1- and 3-chlorine moments should result in a moment equal to that of one, 1.55. However, the three adjacent chlorines give approximately double the opportunity for lowering of moment by induction that is given by two adjacent chlorines and the moment is lowered from 1.55 to 0.65.

At first glance, it would appear that the moment of pentachlorobenzene in Table II should be the same as that of the 1,2,3,5-tetrachlorobenzene, the pair of chlorine moments on one side of the ring cancelling the pair on the opposite side leaving the moment of the central 3-chlorine to determine that of the molecule. However, the 2- and 4-chlorine moments are reduced by the inductive effects of the 1- and 5-chlorines and, consequently, exert a somewhat reduced inductive effect upon the central 3-chlorine, which, therefore, gives a higher moment to the molecule than that found for 1,2,3,5-tetrachlorobenzene. As pentachlorobenzene differs from the two preceding compounds in Table II only in lacking a methyl or ethyl group, one would expect the moments of these latter compounds to be about 0.88 + 0.35 = 1.23, but they are about 0.3 higher.

The moment of 1,2,3,4-tetrachlorobenzene in Table II can be treated as made up of two vectors with a 120° angle between them and a value equal to that of *o*-dichlorobenzene 2.27, which is reduced 0.41 by the induction between the two chlorines. The resultant of the two vectors 2.27 is, of course, 2.27, but their value will be reduced by the induction between the 2- and 3-chlorines. A reduction of 0.4 gives close agreement with the observed moment 1.90. The apparently small and actually zero moments found for the symmetrical molecules of trichloromesitylene or 1,3,5-trimethyl-2,4,6-trichlorobenzene, and dichlorodurene, or 1,2,4,5-tetramethyl-3,6-dichlorobenzene, indicate that the atomic polarizations of these poly-substituted benzenes are small, probably not over 2 cc. The moment value of 2,4,6-trichlorotoluene, which should be the same as that of toluene in the absence of mutual effects between the methyl group and the chlorines, is higher than that of toluene by an amount which may easily arise from the small atomic polarization.

In the molecule of trichloropseudocumene, or 1,2,5-trimethyl-3,4,6-trichlorobenzene, absence of induction would leave a moment equal to that of *p*-chlorotoluene 1.90. The observed value 1.83 is slightly lower than this, though not distinguishable from the moment of pentamethylchlorobenzene. One would expect the moment to be reduced more than 0.07 by the induction between the 3- and 4-chlorines. Indeed, if the resultant of these two chlorine moments is taken as equal to the moment of *o*-dichlorobenzene 2.27, the moment calculated for the molecule is 1.54, 0.3 lower than the observed as in the cases of methyl- and ethylpentachlorobenzene.

The moment of tetrachloro-*o*-xylene should be equal to the sum of the moments of 1,2,3,4-tetrachlorobenzene 1.90 and *o*-xylene, 0.5 observed, 0.61 calculated. If the calculated value of *o*-xylene is used, the sum obtained is 0.13 lower than the observed value 2.64. The moment of 4,5-dichloro-*o*-xylene should similarly be equal to the sum of the moments of *o*-dichlorobenzene and *o*-xylene, 2.27 + 0.61 = 2.88. The observed value is higher than this by 0.13. In other words, the tetrachloro-*o*-xylene and the 4,5-dichloro-*o*-xylene moments differ from each other by just the difference between the moments of

1,2,3,4-tetrachlorobenzene and *o*-dichlorobenzene, as they should, but both are slightly higher than the calculated values. Similarly, the moment of 4,5-dibromo-*o*-xylene[13] 2.86 is higher than the value calculated as the sum of the moments of *o*-dibromobenzene and *o*-xylene, 2.00 + 0.61 = 2.61, but the observed moment of 4-bromo-*o*-xylene[13] 2.07 is identical with the calculated value. In 3,4,5-trichloro-*o*-xylene, the moment due to the three chlorines may be calculated roughly by adding 1.55 to the previously mentioned moment of 1,2,3,5-tetrachlorobenzene 0.65. Resolution of the resultant value 2.20 and the moments due to the two methyl groups gives an approximate value 2.74, which is higher than the observed value 2.46 by no more than its possible error. Dichloroprehnitene, or 1,2,3,4-tetramethyl-5,6-dichlorobenzene, should have the same moment as 4,5-dichloro-*o*-xylene. The observed value is 0.08 lower than this latter and only 0.05 higher than the calculated value. As there was originally some uncertainty as to the composition of a substance subsequently found to be 4,6-dichloro-*m*-xylene, the data on it are omitted from Tables I and II. The moment value observed for it, 2.30, is 0.40 higher than the value calculated as the resultant of the individual methyl and chlorine moments.

In the absence of complicating effects, the moment of dinitroprehnitene, or 1,2,3,4-tetramethyl-5,6-dinitrobenzene, should be equal to that of *o*-dinitrobenzene 6.00 plus the resultant 0.61 calculated for two methyl groups ortho to each other. The observed value 6.86 is slightly higher than this calculated value 6.61, although, for a reason to be discussed presently, one might expect it to be slightly lower. Birtles and Hampson[12] have shown that the moments of nitrodurene and aminodurene are lower than those of the corresponding benzene derivatives and close to those of the corresponding alkyl compounds. The moments of aniline and nitrobenzene, through resonance, receive contributions from highly polar structures in which the nitrogen is linked to the ring by a double bond, with the two other atoms of the group lying in the plane of the ring. Birtles and Hampson conclude that the steric repulsion of the adjacent methyl groups in the durenes tends to prevent the atoms attached to the nitrogen from lying in the plane of the ring and, therefore, reduces the contributions from the highly polar structures. No such reduction is evident, at first glance, in the moment of dinitroprehnitene. The moment of *o*-dinitrobenzene is lowered about 13% below its calculated value, as is also the moment of *o*-chloronitrobenzene, while the moment of *o*-dichlorobenzene is lowered 15% below its calculated value. This difference in lowering is far less than in the case of nitroform and chloroform, in the former of which the lowering below the calculated value is 15% as compared to 44% in the latter.[14] As consideration of the dimensions of the nitro and the methyl groups leads to the conclusion that steric repulsion between the two coplanar nitro groups in *o*-dinitrobenzene would be much greater than that between a methyl group and a nitro group in the plane of the ring, it would appear that the 13% reduction of the moment of *o*-dinitrobenzene below the calculated value may be due, to a considerable extent, to the reduction by steric repulsion of the contribution from the coplanar, highly polar structure. Unless the steric repulsion between the two nitro groups were so great that the addition of a methyl group on each side did not increase the steric effect, one would expect a further lowering of the nitro moments in dinitroprehnitene, which is not observed. Further evidence of the lowering of the nitro moment by the proximity of methyl groups is given by the moment of nitromesitylene 3.65 as compared to 4.00 for nitrobenzene and 3.39 for nitrodurene. A slight lowering is also suggested by the fact that the observed moment of *o*-nitrotoluene 3.66 is lower than the calculated value 3.84, while the observed value of *m*-nitrotoluene 4.17 agrees with the calculated 4.18, and the observed value of the para compound 4.44 is higher than the calculated 4.35. The repulsive effect probably should be less in nitromesitylene than in nitrodurene, where the *o*-methyl groups are pushed somewhat toward the nitro group by the methyls on the next carbons, and obviously should be much less in *o*-nitrotoluene, where, however, the apparent lowering may be due, at least in part, to experimental error.

It is evident that the agreement between the observed and calculated values for these polysubstituted benzenes is fairly good, although the observed values tend to be a little higher than the calculated when the latter are unaffected by in-

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[13] Sidgwick and Springall, *J. Chem. Soc.*, 1532 (1936).

[14] Lewis and Smyth, THIS JOURNAL, **61**, 3067 (1939).

duction. The toluene moment 0.35 used for the methyl group would seem the most logical value, but, as pointed out previously, it is not impossible that this moment should be as high as 0.45. If this higher value is used for the methyl group moment, some of the calculated values become higher than the observed and the difference between the two is no longer always in the same direction. The moments of pentachlorotoluene and pentachloroethylbenzene, 1.55 and 1.50, still remain appreciably higher than the value 1.33 calculated by adding the methyl group moment 0.45 to the moment of pentachlorobenzene. The discrepancy might be explained by a small lowering of the moment of pentachlorobenzene through a slight bending of the chlorine bonds by steric repulsion between the chlorines. The replacement of the one hydrogen by the larger methyl or ethyl would prevent or even slightly reverse this bending but no such effect is apparent in the relation of the moment of tetrachloro-*o*-xylene to that of 1,2,3,4-tetrachlorobenzene, where it should occur to a slightly smaller extent. Similar discrepancies have been noted in the cases of trichloropseudocumene and of the slightly doubtful 4,6-dichloro-*m*-xylene. It is possible that the somewhat better agreement obtained with the higher value 0.45 for the methyl group moment is not due to incorrectness of the toluene moment 0.35, but is due to reinforcement of the methyl moment by interaction through the ring with the other substituent groups. It may be concluded, however, that, in view of experimental errors and of possible small variations in the effect of solvent upon the moment values, the differences between the observed and calculated values of the moments are too small to give definite evidence of any effects of resonance in the methyl- and chlorine-substituted benzenes other than those occurring in the mono-substituted compounds.

The effects of resonance are so great in nitrobenzene with its large moment that their influence upon the chlorobenzene resonance is apparent in the moment value of *p*-chloronitrobenzene 2.78 found for the vapor,[3] which is 0.26 higher than the value calculated as the difference between the vapor values for chlorobenzene and nitrobenzene. The contribution of one of the polar forms due to each substituent is increased by the presence of the other as in the familiar case of *p*-nitroaniline, where the effect is much greater. The observed value for *m*-chloronitrobenzene vapor[3] 3.69 agrees with the calculated 3.68, as does that of *m*-dichlorobenzene previously noted, and the same is approximately true of the solution value of *m*-nitroaniline in the literature, while resonance again increases the moment of *o*-nitroaniline. Although, as previously concluded, the data in this paper fail to establish definitely the existence of the interaction of resonance effects of methyl and chlorine groups upon the ring, they suggest the possibility of a small increase in moment through the mutual effects of para-substitution upon resonance.

In conclusion, the writers wish to express their gratitude to Dr. B. S. Biggs of the Bell Telephone Laboratories, who prepared the compounds here discussed, and to Dr. S. O. Morgan of the same Laboratories, through whose kindness they were made available for our measurements.

Summary

The dipole moments of fourteen tetra-, penta-, and hexa-substituted benzenes with chlorine and the methyl and nitro groups as substituents have been measured in dilute solutions in benzene. The values are compared with those calculated as the vector sums of the moments of mono-substituted benzenes and the effect of induction between groups is taken care of by using the moment of a di-, tri-, or tetra-substituted molecule as a single vector. On the whole, satisfactory agreement is obtained between the observed and the calculated results. The alteration in the moment due to one group produced by the resonance effects of another group is evident in *p*-chloronitrobenzene, but is too small to detect with certainty in these results where methyl and methyl, methyl and chlorine, or chlorine and chlorine are the groups involved, although an indication of a possible small increase in moment due to such effects is given.

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