Induction and Dipole Moment in Chloro and Nitroparaffins

R. H. Wiswall Jr. and C. P. Smyth

Pauling[7] to give rise to a trigonal plane structure, a pyramidal structure also being possible but less stable because of repulsive forces.[8] The larger size of the aluminum atom would make these repulsive forces less in the $(CH_3)_3Al$ than in the $(CH_3)_3B$ molecule, thereby increasing the stability of a possible pyramidal structure. If the pyramidal structure gave the tetrahedral angle 110° to the $C-Al-C$ valence angle, the $Al-CH_3$ moment would be the same as that roughly calculated for the molecule, 1.6×10^{-18}, and the $Al-C$ bond moment, which presumably acts in the opposite direction to the $H-C$ moment, would be 1.6 increased by the estimated value 0.3 of the $H-C$ moment, or 1.9×10^{-18}. Reduction in the size of the $C-Al-C$ valence angle reduces the value calculated for the $Al-C$ moment. If the $C-Al-C$ angle is 90°, the value calculated for the $Al-C$ bond moment is 1.2×10^{-18}, while

if the angle is greater than 110°, the $Al-C$ bond moment is greater than 1.9×10^{-18}. These very rough values estimated for the $Al-C$ bond moment are considerably smaller than one would expect for the aluminum-halogen bond moments and are consistent with the small magnitude of moment and predominantly covalent character attributed to metal-carbon bonds.[9]

Because of the considerable importance of the structures of aluminum compounds, it has seemed desirable to present these experimental data in spite of the difficulties which molecular association introduces into their interpretation. Although these difficulties are such as to render any conclusions somewhat uncertain, the data do indicate a strong probability that the monomeric trimethylaluminum molecule has a pyramidal structure and that the aluminum-carbon bond is largely covalent.

[7] Pauling, J. Am. Chem. Soc. 53, 1367 (1931).
[8] G. E. Kimball, J. Chem. Phys. 8, 188 (1940).

[9] G. L. Lewis, P. F. Oesper and C. P. Smyth, J. Am. Chem. Soc. 62, 3243 (1940).

Induction and Dipole Moment in Chloro- and Nitroparaffins

R. H. WISWALL, JR. AND C. P. SMYTH
Frick Chemical Laboratory, Princeton University, Princeton, New Jersey
(Received January 9, 1941)

The dielectric constants of the vapors of the butyl chlorides, methyl chloroform, nitromethane, α- and β-nitropropane, and 2-methyl-2-nitropropane have been measured over a range of temperature and pressure and used to calculate the dipole moments of the molecules of these substances. The dipole moment increases from normal to secondary to tertiary butyl chloride much less than indicated by the apparent moments previously measured in solution, it being shown that the apparent solution values for the primary and secondary compounds are lowered by solvent effect. The moments found for α- and β-nitropropane and 2-methyl-2-nitropropane are indistinguishable from one another, but are slightly larger than that of nitromethane. Examination of the molecular models shows that the moment differences found are approximately those to be expected from the inductive effects, with the exception of the large difference between chloroform and methyl chloroform where it can only be said that induction is a major cause of the difference.

INDUCTION is often such an important factor in the interpretation of dipole moment data that it has seemed desirable to check up on certain ideas as to induction effects which were originally based upon moment values determined in solution and thus subject to the uncertainties introduced by solvent effects. This checking up process has been carried out by measuring the dipole moments in the vapor state of the four butyl chlorides and methyl chloroform previously measured in solution and of four nitroparaffins, two of which had previously been measured as vapors. The measurements were carried out with the modified heterodyne beat apparatus previously described,[1-3] the

[1] K. B. McAlpine and C. P. Smyth, J. Am. Chem. Soc. 55, 453 (1933).
[2] J. M. A. de Bruyne and C. P. Smyth, J. Am. Chem. Soc. 57, 1203 (1935).
[3] R. H. Wiswall and C. P. Smyth, J. Chem. Phys. 9, 352 (1941).

dielectric constant being determined at each temperature over a wide range of pressure so as to eliminate the effects of deviations from the ideal gas law. Air and *n*-butyl chloride were used in calibrating the apparatus, the capacity of the gas-containing condenser being determined finally from measurements on the *n*-butyl chloride vapor, which had been accurately determined previously.[4]

PURIFICATION OF MATERIALS

The chloroparaffins, obtained from the Eastman Kodak Company, were purified by thorough washing with water or sulfuric acid followed by sodium carbonate solution, drying over calcium chloride, and fractional distillation. The *i*-butyl chloride was purified by Dr. Anthony Turkevich in this laboratory. The nitromethane was part of an old sample from the Eastman Kodak Company, and the two nitropropanes were very kindly given us by the Commercial Solvents Corporation. These substances were dried over calcium chloride and fractionally distilled. The 2-methyl-2-nitropropane was given us by Professor R. H. Ewell of Purdue University. It was used without further purification. The boiling points and refractive indices for the sodium *D* line at 20° determined for the compounds as criteria of purity are given in Table I, which also lists the molar refractions, MR_D.

EXPERIMENTAL DATA

The polarizations P calculated from capacity-pressure curves at each absolute temperature T are listed in Table II. As the tendency of some

TABLE I. *Boiling points, refractive indices, and molar refractions.*

	B.p., °C	$n^{20}D$	MR_D
n-C$_4$H$_9$Cl	78	1.4023	25.5
i-C$_4$H$_9$Cl	68.2	1.3983	25.4
s-C$_4$H$_9$Cl	68.1	1.3969	25.7
t-C$_4$H$_9$Cl 1st sample	50.6	1.3853	
2nd sample	50.8 (756 mm)	1.3858	25.9
CH$_3$CCl$_3$	74.5 (767 mm)	1.4384	26.1
CH$_3$NO$_2$	101.0	1.3824	12.5
n-C$_3$H$_7$NO$_2$	130.9 (753 mm)	1.4003	21.6
i-C$_3$H$_7$NO$_2$	120.1 (763 mm)	1.3949	21.6
t-C$_4$H$_9$NO$_2$	122–124	1.4015	26.1

[4] C. P. Smyth and K. B. McAlpine, J. Chem. Phys. **3**, 347 (1935).

TABLE II. *Polarizations and dipole moments.*

T, °K	P	MOMENT ($\times 10^{18}$) (USING MR_D)	(USING $P_E + P_A$)
i-Butyl chloride			
345.2	99.1	2.05	2.00
360.0	95.7	2.04	2.00
368.0	93.9	2.04	1.99
387.5	92.0	2.06	2.01
406.5	87.8	2.04	1.99
	Mean value = 2.04		2.00
s-Butyl chloride			
335.9	106.3	2.11	2.07
351.9	102.6	2.11	2.07
371.2	99.6	2.12	2.08
392.0	95.3	2.12	2.08
	Mean value = 2.12		2.08
t-Butyl chloride 1st sample			
314.1	114.1	2.13	2.10
339.7	104.6	2.10	2.06
t-Butyl chloride 2nd sample			
324.3	111.1	2.13	2.10
340.8	108.1	2.15	2.11
341.9	109.4	2.17	2.13
354.1	101.4	2.10	2.06
	Mean value = 2.13		2.09
Methyl chloroform			
335.8	83.9	1.79	
347.7	81.5	1.78	
372.0	77.4	1.77	
398.6	73.1	1.75	
	Mean value = 1.77		
Nitromethane			
367.8	215.4		
421.0	190.9		
α-Nitropropane			
382.0	242.5	3.73	3.68
404.4	230.5	3.74	3.68
408.9	227.7	3.72	3.67
421.2	223.8	3.74	3.69
438.0	210.8	3.69	3.64
457.0	204.4	3.71	3.65
	Mean value = 3.72		3.67
β-Nitropropane			
391.8	237.4	3.73	3.68
406.9	231.8	3.75	3.70
422.0	218.4	3.71	3.64
439.0	213.3	3.72	3.66
454.9	208.3	3.74	3.68
	Mean value = 3.73		3.67
2-Methyl-2-nitropropane			
379.1	246.9	3.71	3.66
398.9	238.9	3.74	3.69
416.4	227.7	3.72	3.66
432.5	219.5	3.71	3.65
449.3	210.8	3.69	3.64
	Mean value = 3.71		3.66

of the compounds to decompose at high temperatures limited the range of temperature over which the measurements could be made, the dipole moment μ was calculated at each temperature from the difference between P and MR_D. As an atomic polarization $P_A = 3.8$ had been found for n-butyl chloride,[4] values were also calculated for the moments of the butyl chlorides by using, instead of MR_D, the total induced polarization $P_E + P_A = 28.5$ previously found for n-butyl chloride and similar induced polarization values calculated for the nitroparaffins by using the atomic polarization value 6.1 previously found for nitromethane.[5] The two slightly differing sets of moment values are listed for comparison in Table II, the mean value being listed at the bottom of each column. The true value for each substance presumably lies between these two mean values, but should not, in any event, be higher than the value calculated by the use of MR_D by more than the probable experimental error 0.02×10^{-18}. The values calculated by the use of MR_D are, therefore, adopted as correct and used in Table III for comparison with other values determined in this laboratory and elsewhere and taken from the literature. Only two values of the polarization are given for nitromethane as they were redetermined merely as a check. The values interpolated for these temperatures from the data of Smyth and McAlpine[5] are 215.0 and 190.2, in excellent agreement with the values obtained here.

DISCUSSION OF RESULTS

As we are primarily concerned with the interpretation of small differences among the observed dipole moments, it is desirable to compare their accuracy with that of measurements on alkyl halides previously made in this laboratory[6] and with that of determinations of Groves and Sugden[7] upon several homologous series. These values are collected in Table III for comparison as well as interpretation, the values determined by Smyth and McAlpine being followed by an M, those of Groves and

[5] C. P. Smyth and K. B. McAlpine, J. Am. Chem. Soc. 56, 1697 (1934).
[6] C. P. Smyth and K. B. McAlpine, J. Chem. Phys. 2, 499 (1934).
[7] L. G. Groves and S. Sugden, J. Chem. Soc. 158 (1937).

TABLE III. *Moments* $(\times 10^{18})$ *of homologous series in the vapor state.*

	F	Cl	Br	I	NO₂
CH₃	1.81M	1.87G	1.78M	1.59M	3.50M
			1.79G	1.64G	3.54G
C₂H₅	1.92M	2.05G	2.02M	1.90M	3.58G
			2.01G	1.87G	
n-C₃H₇		2.10G	2.15G	2.01G	3.57G
					3.72
n-C₄H₉		2.11G	2.15G	2.08G	3.55G
		2.09M			
n-C₅H₁₁		2.12G			
n-C₇H₁₆			2.15M		
i-C₃H₇		2.15G	2.19G		3.73
i-C₄H₉		2.04			
s-C₄H₉		2.12	2.20G		
t-C₄H₉		2.13			3.71

Sugden by a G and those obtained in the present investigations and reported in Table II being left unmarked.

The values of Groves and Sugden for methyl, ethyl, and n-propyl chloride were recalculated from the measurements of other investigators on the assumption, employed in calculating from their own experimental data, that $P_E + P_A = 1.05 MR_D$. The values of Smyth and McAlpine were obtained from the slopes of the $P - 1/T$ curves, except for the n-butyl chloride and n-heptyl bromide values, which were obtained from the difference $P - MR_D$. The n-butyl chloride value was originally obtained from the $P - 1/T$ curve as 2.04, but the P_A value given by this curve was sufficient to lower it appreciably in comparison to values calculated by the other method. The higher value obtained from $P - MR_D$ is, therefore, given in Table III for comparison with that obtained by Groves and Sugden from $P - 1.05 MR_D$. The values of P_A obtained by Smyth and McAlpine for the methyl and ethyl halides are so near to the allowances for this quantity made by Groves and Sugden that no discrepancy between the two sets of values can arise from this source. It is evident from the calculations of moment in two ways in Table II that Groves and Sugden's method of subtracting $1.05 MR_D$ instead of MR_D from the polarization would lower the moment by only 0.01 or 0.02×10^{-18} below the value obtained by subtracting MR_D. The probable error given by Groves and Sugden for their results is 0.01×10^{-18}, but as they have sometimes taken as the correct value a mean of their value and others in the

literature giving a result 0.02 different from theirs, and as their several values for a substance show much the same variation as those in Table II, their probable error may be taken to be the same as that in the results of Table II. It would not, therefore, be surprising to encounter occasionally a difference between values for the same substance as great as 0.04, which might be increased by 0.01 or 0.02 by use of $1.05MR_D$ instead MR_D. In order to make the values in Table III a direct comparison of three consistent sets of measurements, the values quoted from the paper of Groves and Sugden are those calculated wholly from their own measurements rather than the occasionally slightly different mean values which they estimated from their own and literature values. The greatest difference between the value of Groves and Sugden for any of the five alkyl halides previously measured by Smyth and McAlpine and that found by the latter is seen to be 0.05 and the average difference is only 0.02. There is, however, a noticeable discrepancy among the values for the nitroparaffins. The value found in the present investigation for α-nitropropane, which is indistinguishable from those found for β-nitropropane and 2-methyl-2-nitropropane, is 0.15 higher than the value found by Groves and Sugden for this compound, which, in their measurements, is very close to the values found for nitromethane, nitroethane and α-nitrobutane. Because of this discrepancy, a few measurements were made upon nitromethane, the close agreement previously noted being obtained with the results of Smyth and McAlpine,[5] which, when calculated with MR_D instead of the larger value of $P_E + P_A$ containing $P_A = 6.1$, give a value only 0.04 lower than that of Groves and Sugden. The good agreement between the boiling point, 130.9° at 753 mm, of the α-nitropropane used in the present investigation and the boiling point, 131.4° at 766 mm, of the material used by Groves and Sugden provides evidence against impurity as the source of the discrepancy.

The increases in moment of the alkyl halides and some other alkyl compounds on going from the methyl to the ethyl compound and of the solution values for the butyl halide moments on going from primary to secondary to tertiary have been attributed to dipoles induced by the carbon-halogen dipole in the groups immediately attached to the primary carbon.[8] As is evident in Table III, the methyl-ethyl moment difference increases by about 0.07×10^{-18} for each change from fluorine to chlorine to bromine to iodine. The smaller increase from the ethyl to the n-propyl halides, which was not evident in the earlier values for the chlorides, also increases by about the same amount on the change from chlorine to bromine, which is about the same as that from bromine to iodine. Any increase in moment on going from the n-propyl to the n-butyl halides is too small to be evident except in the case of the iodide, where the difference is again 0.07×10^{-18}. The long n-heptyl bromide molecule has the same moment as the n-butyl and n-propyl bromide molecules. Groves and Sugden[7] explained qualitatively the change in the increase of moment for the different halides in terms of the size of the halogen atom and an effect of the hydrocarbon chain upon the field of the primary dipole, but no quantitative explanation has been advanced. Their careful calculation[9] of inductive effects, which involves the fundamental uncertainties inherent in earlier calculations, gives a moment increase from methyl to ethyl chloride of 0.11×10^{-18} as compared to 0.18 observed, for the bromides, an increase of 0.11 calculated as compared to 0.21 observed, and, for the iodides, 0.10 as compared to 0.23 observed. Their calculated increase from ethyl chloride to i-propyl chloride, which is caused by increase in the amount of polarizable matter within the effective range of the $C-Cl$ dipole, is 0.07 as compared to an observed 0.10, and, for the bromides, the calculated increase is 0.06 as compared to 0.18 observed. The increase in moment from normal to secondary butyl chloride should be approximately the same as that from n-propyl to i-propyl. The value observed in the present investigation is 0.03 as compared to 0.05 for the change from n-propyl to i-propyl chloride and for the change from normal to secondary butyl bromide observed by Groves and Sugden. The further increase observed from secondary to tertiary butyl chloride

---

[8] C. P. Smyth, *Dielectric Constant and Molecular Structure* (The Chemical Catalog Company, New York, 1931), pp. 75, 102.

[9] L. G. Groves and S. Sugden, J. Chem. Soc. 1992 (1937).

is only 0.01, an amount too small to establish the existence of the increase which is to be expected because of the further increase in the amount of polarizable matter within the effective range of the C−Cl dipole. The increase from ethyl to i-propyl chloride calculated by Groves and Sugden is approximately $\frac{2}{3}$ of that calculated for the methyl to ethyl increase, while the observed increases, though larger, are in the same ratio as the calculated. The moment induced in each methyl group added to the primary carbon has a considerable component perpendicular to the direction of the axis of the C−Cl dipole. When two methyl groups are present as in s-butyl chloride, these two components, making a wide angle with each other, have a resultant about equal to the contribution of the one component in ethyl chloride. In t-butyl chloride, these three components perpendicular to the C−Cl direction cancel one another so that the increase from the primary to the secondary compound should be less than that from methyl to ethyl and the increase from the secondary to the tertiary compound should be less than that from the primary to the secondary.

The much larger size of the increase in the apparent moment values observed in solution, in benzene or heptane, 1.97 for n-butyl chloride, 2.09 for s-butyl chloride, and 2.15 for t-butyl chloride was due to solvent effect. It has been shown by Higasi[10] and by Frank[11] that, when the axis of the molecular dipole lies in the longest axis of the molecule, the moment observed for the molecule in solution is lower, because of inductive effects, than that observed in the vapor state, while, if the dipole axis lies perpendicular to the longest axis of the molecule, the apparent moment value observed in solution is higher than that observed for the gas. Because of possible rotation around the C−C bonds in the butyl chlorides, it is difficult to establish with any precision the position of the longest axis of the molecule relative to the principal dipole, that in the C−Cl bond, but it appears fairly certain that the dipole is, on the average, more nearly parallel than perpendicular to the

longest molecular axis. Consequently, the apparent moment observed in solution should be lower than the gas value, as found. Change from the primary to the secondary butyl chloride lessens the difference between the molecular dimensions in different directions and, therefore, lessens the difference between the gas value of the moment and the apparent solution value. Finally, the t-butyl chloride molecule is so nearly spherical in form that the molecular dimensions are nearly the same in all directions. Consequently, the solution value of the moment should be indistinguishable from the gas value as found.

The solution values[8] for the moments of i-butyl chloride, bromide and iodide are identical with those for the corresponding normal compounds. Shortening of the molecule through branching of the chain may have lessened the lowering of the apparent moment by solvent effect, raising the solution values of the i-butyl halides to equal those for the n-butyl and thus accounting for the failure to observe differences like the small difference between the gas values for i-butyl and n-butyl chloride in Tables II and III. The branching of the chain in the i-butyl group is so far from the C−Cl dipole that one would, at first glance, expect it to have very little effect upon the moment of the molecule, the change, if any, being a slight increase due to the added amount of polarizable material near the limit of the effective inductive action of the C−Cl dipole. The small but appreciable decrease observed in the i-butyl chloride moment as compared to that of n-butyl chloride is, however, not inconsistent with the appearance of the molecular model, for, of the different positions possible for the two methyl groups through rotation around the carbon-carbon bonds of the molecule, a large fraction places these groups in the neighborhood of the C−Cl dipole where they would make such angles with the axis of the dipole that the moments induced in them would oppose that of the inducing dipole and thus tend to reduce the observed molecular moment. Such an inductive effect probably accounts for the lowering of the moment of i-butyl alcohol 0.05×10^{-18} below that of n-butyl alcohol.[7]

The moment 1.77 obtained for methyl chloroform in Table II is about 0.8×10^{-18} higher than

[10] K. Higasi, Sci. Pap. Inst. Phys. Chem. Res. (Tokyo) 28, 284 (1936).
[11] F. C. Frank, Proc. Roy. Soc. (London) A152, 171 (1935).

that of the chloroform molecule. It should be higher than the latter because of the inductive action of each of the three $C-Cl$ dipoles upon the methyl group. On the other hand, these three dipoles, because of their mutual inductive action, should be somewhat smaller than the $C-Cl$ dipoles in methyl and ethyl chloride, thus accounting for the much lower moment of chloroform as compared to methyl chloride. The moment induced in the methyl group by each of the three $C-Cl$ dipoles should, therefore, be smaller than the similarly induced moment in the methyl group of ethyl chloride. Moreover, each of these induced moments will have a component perpendicular to the $C-C$ line and, in methyl chloroform, these three components perpendicular to the $C-C$ line will cancel one another. The increase in moment of methyl chloroform over chloroform should, therefore, be considerably less than three times the increase, 0.18×10^{-18}, from methyl to ethyl chloride. These considerations have neglected possible change in the small $H-C$ bond moment, although Raman spectra show a slightly tighter binding of the $H-C$ bond in chloroform than of those in the methyl group in methyl chloride.[12] Electron diffraction shows no abnormality in the $C-Cl$ bonds in chloroform[13] such as has been found in the carbon-halogen bonds in the fluoromethanes and fluorochloromethanes.[14] Increases in moment analogous to that from chloroform to methyl chloroform have been found in the solution values for 1,1-dichloroethane, 1,1-dichloropropane, and 2,2-dichloropropane[15] as compared to that for methylene chloride, the increases again being somewhat larger than those estimated. The roughly quantitative treatment of these increases in moment does not establish induction as the only cause of the increases, but it does indicate it to be a major cause.

The calculations of Groves and Sugden[9] of the inductive effects in nitromethane and nitroethane, in which they use a single resultant moment for the $C-N$ and the two $N-O$ dipoles, are in agreement with the small rise which they observe from the methyl to the ethyl compound. This is in contrast to the markedly higher observed than calculated values in the case of the alkyl halides. In view of the smallness of the rise from the methyl to the ethyl compound in Table III, the absence of rise in the values of Groves and Sugden for the propyl and butyl compounds is to be expected. However, their treatment of the small $C-N$ dipole and the two large $N-O$ dipoles as a single resultant dipole introduces an added element of uncertainty not present in their calculations of inductive effects in the alkyl halides, so that there should be a possibility of error in these calculations even greater than those in the treatment of the alkyl halides, where the calculated increases were considerably smaller than the observed. The much larger increase in moment from nitromethane to α-nitropropane observed in the present investigation is not, therefore, to be regarded as necessarily conflicting with structural considerations, although the reason for the difference between this value and that found by Groves and Sugden is not apparent. Examination of models of these molecules shows that the two methyl groups in β-nitropropane and the three methyl groups in 2-methyl-2-nitropropane must, on the average, spend a good part of the time in positions at such angles to the axis of the nearer of the two $N-O$ dipoles that this will induce moments in them partially opposing the resultant molecular moment. The amount of this opposition of the induced moments could be quite sufficient to cancel the contributions of moments induced in the direction of the principal moment. It is reasonable, therefore, that the molecules of α-nitropropane, β-nitropropane, and 2-methyl-2-nitropropane should have moments indistinguishable from one another, although these considerations are not sufficiently exact to predict their identity.

[12] J. H. Hibben, Chem. Rev. **18**, 14 (1936).
[13] L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936).
[14] L. O. Brockway, J. Phys. Chem. **41**, 747 (1937).
[15] P. M. Gross, Physik. Zeits. **32**, 587 (1931).