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Citation: *The Journal of Chemical Physics* **17**, 1174 (1949); doi: 10.1063/1.1747138

View online: <http://dx.doi.org/10.1063/1.1747138>

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Dipole Moment and Restricted Rotation in Some Chlorinated Hydrocarbons*

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(Received December 15, 1948)

Measurements of the variation of gas phase dipole moment with temperature of six chlorinated hydrocarbons are described. 1,2-dichloropropane, and, to a very small extent, 2,3-dichloropropene and 1,1,2-trichloroethane display a dependence of dipole moment on temperature. 1,4-dichlorobutane and the two isomers of 1,3-dichloropropene have dipole moments constant over the temperature range investigated. The results are analyzed both by adopting simple parametric functions to represent the potential hindering intramolecular rotation, and by computations of intramolecular energies.

RESTRICTED internal rotation can be studied in many ways, such as by electron diffraction,^{1,2} infra-red and Raman spectra,³ thermochemical measurements linked with statistical thermodynamical calculations,⁴ and by the temperature variation of the dipole moments.⁵ Of these, the latter is the most direct when applicable, since the observed phenomenon is an unambiguous function of the internal rotation. Because only relatively few vapor measurements of moment as a function of temperature exist in the literature,⁶⁻¹³ it was thought worth while to investigate some of the chlorinated ethanes, as well as some dichlorinated methyl- and methylene-substituted ethanes. A preliminary note on our experimental results has already been published.¹⁴

EXPERIMENTAL

The heterodyne beat apparatus used to measure the dielectric constants of the vapors has been described elsewhere.¹⁵ The pressure of the vapor in the dielectric cell is increased by using air pressure to force liquid up one leg of a U-tube into a heated region in which it vaporizes. Similarly, to decrease the pressure of the vapor, the air pressure is decreased on the other side of the liquid in the U-tube. The slope of the capacitance-

pressure curve was determined, using some six pressures, or the two-point method was used and several determinations made and the average taken.

All the compounds were purified by careful distillation over a suitable desiccant through a four-foot packed column, and fractions boiling over 0.1° range or less were used in the measurements. The 1,1,2-trichloroethane and 1,4-dichlorobutane were obtained from Eastman Kodak; the 2,3-dichloropropene was received from Columbia Organic Chemicals Company, the 1,2-dichloropropane, from the Paragon Testing Laboratories, and the two isomers of 1,3-dichloropropene, from Halogen Chemicals Company. The dielectric cell was calibrated with the vapors of chlorobenzene, ethyl bromide, and nitrobenzene. Molar refractions were computed from refractive indices and densities of the liquids in the literature; these were measured when literature values were lacking.

RESULTS

Table I presents the molar refractions, and the polarizations and dipole moments *versus* temperatures for the six compounds examined. The dipole moments, μ , were computed from the polarizations, P , by the well-known relationship, $\mu = 0.01281 \times 10^{-18} [(P - R_D)T]^{\frac{1}{2}}$, where R_D is the molar refraction for the D sodium line and T is the absolute temperature. The moment-temperature relationships for 1,1,2-trichloroethane, 1,2-dichloropropane, and 2,3-dichloropropene are shown graphically in the A -curves of Fig. 1, in which are also shown for comparison the data of Zahn⁸ for 1,2-dichloroethane, the other data for this substance in the literature^{9,13} being in essential agreement with these. In Table II are gathered together the vapor dipole moment measurements for the halogenated ethanes, propanes, propenes, and butane that might be expected to display a variation of dipole moment with temperature and also two similar compounds containing bromine. The table also includes values calculated by the equation of Smyth and Walls^{16,17} for the dipole moment that would be observed if completely free intramolecular

* This work was carried out with the support of the ONR.

¹ P. Debye, *J. Chem. Phys.* **9**, 55 (1941).

² J. Y. Beach and K. J. Palmer, *J. Chem. Phys.* **6**, 639 (1938).

³ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, New York, 1945).

⁴ E. B. Wilson, Jr., *Chem. Revs.* **27**, 17 (1940); K. S. Pitzer, *J. Chem. Phys.* **14**, 239 (1946); Conn, Kistiakowsky, and Smith, *J. Am. Chem. Soc.* **61**, 1868 (1939).

⁵ Smyth, Dornste, and Wilson, Jr., *J. Am. Chem. Soc.* **53**, 4242 (1931); L. Meyer, *Zeits. f. physik. Chemie* **8B**, 27 (1930).

⁶ Ghosh, Mahanti, and Sen Gupta, *Zeits. f. Physik* **54**, 711 (1929).

⁷ Sanger, *Zeits. f. Physik* **32**, 21 (1931).

⁸ C. T. Zahn, *Phys. Rev.* **40**, 291 (1932); **38**, 521 (1931).

⁹ E. W. Greene and J. W. Williams, *Phys. Rev.* **42**, 119 (1932).

¹⁰ C. P. Smyth and K. B. McAlpine, *J. Am. Chem. Soc.* **57**, 979 (1935).

¹¹ R. H. Wiswall and C. P. Smyth, *J. Chem. Phys.* **9**, 356 (1941).

¹² Maryott, Hobbs, and Gross, *J. Am. Chem. Soc.* **63**, 659 (1941).

¹³ Watanabe, Mizushima, and Morino, *Sc. Pap. Inst. Phys. and Chem. Res. No. 1090* **39**, 401 (1942).

¹⁴ R. A. Oriani and C. P. Smyth, *J. Chem. Phys.* **16**, 930 (1948).

¹⁵ R. H. Wiswall, Jr. and C. P. Smyth, *J. Am. Chem. Soc.* **64**, 2212 (1942).

¹⁶ H. Eyring, *Phys. Rev.* **39**, 746 (1932).

¹⁷ C. P. Smyth and W. S. Walls, *J. Am. Chem. Soc.* **54**, 2261 (1932).

rotation existed. The values used for the group moments in these calculations were 1.85×10^{-18} for $-\text{CH}_2\text{Cl}$ in 1,2-dichloroethane, 1,1,2-trichloroethane, and 1,2-dichloropropane,¹⁷ 1.57×10^{-18} for $-\text{CHCl}_2$ in 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane, and 1.85×10^{-18} for $-\text{CH}_2\text{Br}$. Values calculated for the restricting potential energy V_0 as discussed subsequently are given in the last column. The \pm percent given after each value is the average deviation from the mean of the values calculated at different temperatures over the range indicated and is not an estimate of absolute accuracy.

DISCUSSION OF RESULTS

We shall employ two general approaches in the treatment of the data. Firstly, we shall attempt to find a relatively simple mathematical function that will roughly express the net interaction between the rotating groups, and from which the observed dipole moment and its variation with temperature can be deduced. Secondly, we shall attempt to calculate from first principles a curve of potential energy of interaction between the groups as a function of azimuthal configuration, which can then be used either to establish qualitatively the reasonableness of the observed phenomena, or to compute the temperature variation of the dipole moment.

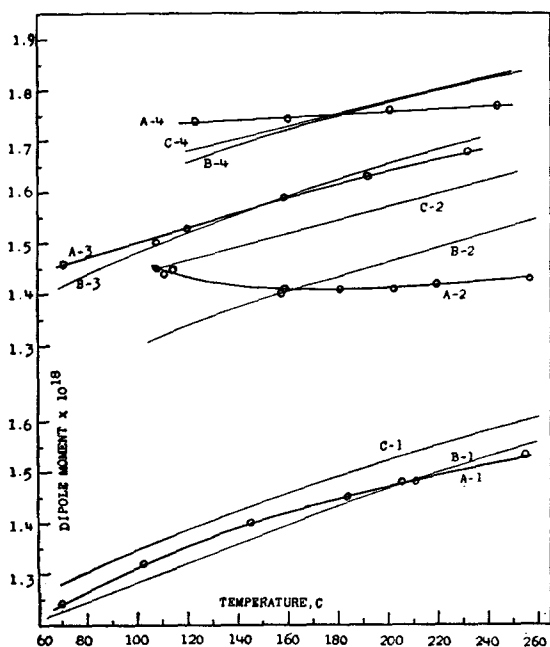


FIG. 1. Temperature dependence of dipole moments of chlorinated hydrocarbons.

A: Experimental curves.
B: Curves calculated from one-parameter analysis.
C: Curves calculated by special functions.

Molecules:

1. 1,2-dichloroethane.
2. 1,1,2-trichloroethane.
3. 1,2-dichloropropane.
4. 2,3-dichloropropane.

¹⁷ C. P. Smyth and K. B. McAlpine, J. Chem. Phys. 1, 193 (1933).

TABLE I. Polarizations, molar refractions, and dipole moments.

Compound	T, °K	P, cc	$\mu (\times 10^{18})$
1,1,2-trichloroethane ($R_D = 25.85$)	381.0	59.4	1.45
	384.4	58.9	1.44
	388.2	59.0	1.45
	431.2	53.6	1.40
	431.8	54.0	1.41
	454.7	52.5	1.41
	476.2	51.4	1.41
1,2-dichloropropane ($R_D = 25.60$)	493.2	55.7	1.42
	530.4	49.5	1.43
	344.7	63.1	1.46
	381.7	61.4	1.50
	393.8	61.8	1.53
	432.2	61.0	1.59
	465.6	60.3	1.63
2,3-dichloropropene ($R_D = 25.49$)	505.7	59.6	1.68
	397.0	72.1	1.74
	434.0	68.2	1.74
	474.7	65.2	1.76
1,3-dichloropropene 104° isomer ($R_D = 25.4$)	517.9	62.4	1.77
	397.2	74.8	1.79
	399.2	74.6	1.79
	478.3	65.5	1.78
112° isomer ($R_D = 25.5$)	395.2	76.0	1.81
	449.7	70.5	1.82
	502.7	65.0	1.81
1,4-dichlorobutane ($R_D = 30.27$)	432.9	99.6	2.22
	468.7	94.8	2.23
	506.7	88.5	2.21

For a 1,2-disubstituted ethane, one can write¹⁹ for the instantaneous dipole moment,

$$\mu^2(\phi) = A + B \cos \phi, \quad (1)$$

where

$$A = m_1^2 + m_2^2 - 2m_1m_2 \cos \theta_1 \cos \theta_2,$$

and

$$B = 2m_1m_2 \sin \theta_1 \sin \theta_2.$$

In these expressions, m_1 and m_2 are the group moments of the polar substituents on the two carbons assumed constant irrespective of internal configuration; these are located at angles θ_1 and θ_2 to the direction of the C—C bond. ϕ is the azimuthal angle between the two group dipoles, zero at the *cis*- and 180° at the *trans*-position. From Eq. (1) it follows that the dipole moment measured for an assembly of molecules is

$$\mu = [A + B \langle \cos \phi \rangle_{av}]^{1/2}, \quad (2)$$

where $\langle \cos \phi \rangle_{av}$, the mean of $\cos \phi$ averaged over all the molecules, is given by

$$\langle \cos \phi \rangle_{av} = \frac{\int_0^{2\pi} \cos \phi \exp[-V(\phi)/RT] d\phi}{\int_0^{2\pi} \exp[-V(\phi)/RT] d\phi}. \quad (3)$$

¹⁹ J. Y. Beach and D. P. Stevenson, J. Chem. Phys. 6, 635 (1938).

TABLE II. Temperature variation of dipole moment and restricting potential energy.

	$t, ^\circ\text{C}$	μ_{obs}	μ_f^*	V_0 (cal./mole)
$\text{Cl}_2\text{HC}-\text{CH}_2\text{Cl}^{\text{18}}$	32-271°	1.12-1.54	2.46	3215 ± 2.9 percent
$\text{BrH}_2\text{C}-\text{CH}_2\text{Cl}^{\text{18}}$	66-163°	1.09-1.28	2.46	3900 ± 1.5 percent
$\text{BrH}_2\text{C}-\text{CH}_2\text{Br}^{\text{9}}$	66-163°	0.94-1.10	2.46	5090 ± 1.6 percent
$\text{Cl}_2\text{HC}-\text{CH}_2\text{Cl}$	105-258°	1.43	2.36	2820 ± 10.5 percent
$\text{Cl}_2\text{HC}-\text{CHCl}_2^{\text{10}}$	128-163°	1.36	2.10	
$\text{ClH}_2\text{C}-\text{CHClCH}_3$	71-235°	1.46-1.68	2.46	2500 ± 2.2 percent
$\text{ClH}_2\text{C}-\text{CCl}=\text{CH}_2$	125-245°	1.74-1.77	2.46	2075 ± 7.7 percent
$\text{ClH}_2\text{C}-\text{CH}_2-\text{CH}_2\text{Cl}$	101-201°	2.07	2.36	
$\text{ClH}_2\text{C}-(\text{CH}_2)_2-\text{CH}_2\text{Cl}$	160-235°	2.22	2.60	

* Calculated for completely free internal rotation.

Here, $V(\phi)$ represents the functional relationship that exists between the intramolecular potential energy and azimuthal angle ϕ , T is the temperature, and R the gas constant. With $V(\phi) = (V_0/2)(1 + \cos\phi)$ as assumed in former papers on this subject,^{19, 20-23} Beach and Stevenson have shown that Eq. (3) can be evaluated analytically as a ratio of Bessel functions with imaginary argument:

$$\langle \cos\phi \rangle_{\text{av}} = \frac{iJ_1(iV_0/2RT)}{J_0(iV_0/2RT)} \quad (4)$$

The value of the parameter V_0 can thus be calculated by means of Eqs. (2) and (4) from an experimental value of the dipole moment at one temperature. This has been done for the substituted ethanes and propanes that show variation of dipole moment with temperature. If the one-parameter potential function assumed is an adequate representation of the actual energy relationship, the parameter for any one molecule should be independent of temperature and deviation from constancy may be taken as a measure of the inadequacy of the assumed potential function. In Table II the last column gives the mean values of V_0 obtained from the moment values at several temperatures, as well as the deviation from constancy expressed as a percentage. The effect of using a larger group moment is to raise the calculated V_0 . Thus, adopting a group moment of 2.03×10^{-18} for $-\text{CH}_2\text{Cl}$, Beach and Stevenson¹⁹ computed a V_0 of 4000 cal./mole for 1,2-dichloroethane.

It is evident from the small percentage variations in V_0 that the simple potential function empirically represents the facts for the disubstituted ethanes and 1,2-dichloropropane. The potential barrier in the 1,2-dihaloethanes increases regularly as bromine replaces chlorine, in qualitative agreement with the expected effect of the larger bulk of the bromine atom. Figure 1B shows the curves for dipole moment against temperature calculated by means of Eqs. (2) and (4), using the mean values of V_0 tabulated in Table II for the chlorinated

hydrocarbons. The agreement between the experimental curves and those calculated is not bad for the 1,2-dichloroethane and 1,2-dichloropropane. In the case of 1,2-dichloroethane, the agreement is about the same if a two-parameter function

$$V(\phi) = V_1 \cos\phi + V_2 \cos 2\phi \quad (5)$$

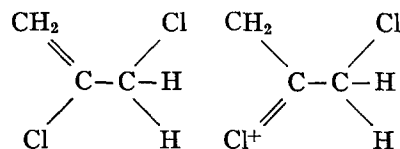
is used, and the effects of the moments of inertia are included as done by Altar²⁴ (see curve C-1 of Fig. 1), a procedure now recognized⁴ as leading to error.

Since such a function as that in Eq. (5) has clearly the incorrect symmetry in the second term for representing the interactions among the hydrogens on one carbon and the chlorine on the other, Gwinn and Pitzer²⁵ have adopted the form

$$V(\phi) = (V_1/2)(1 - \cos\phi) + (V_3/2)(1 - \cos 3\phi), \quad (6)$$

from which they successfully calculate the heat capacity, entropy and dipole moment of 1,2-dichloroethane, using a partition function which is the weighted sum of the partition functions for molecules in the *trans* and in the skew configurations.

The V_0 values from the one-parameter analysis give a satisfactory qualitative explanation for the observed magnitudes and temperature dependence of the dipole moments of 1,2-dichloroethane and 1,2-dichloropropane. However, the simple one-parameter function is not successful in the cases of 2,3-dichloropropene and 1,1,2-trichloroethane as is evident from Fig. 1. The case of 2,3-dichloropropene is complicated by the presence of the double bond whose effect is difficult to evaluate. One group moment is lowered by resonance among structures,



If we regard this effect as approximately independent of the azimuthal configuration of the $-\text{CH}_2\text{Cl}$ group, we may take as the constant group moment of the

$\text{CH}_2 = \text{C} - \text{Cl}$ the gas value of vinyl chloride, 1.44×10^{-18} , instead of the 1.85 used in the calculation of V_0 listed in Table II. This lower value of the group moment gives $V_0 = 725$ cal./mole ± 7 percent for 2,3-dichloropropene, which gives as low a degree of self-consistency as the former calculation. Hence, it is not an improper choice of group moment that produces the poor result, though it may well be the assumption of its constancy with azimuthal angle. In an attempt to find a potential function of the type in Eq. (6) that yields a calculated $\mu-T$ curve in better agreement with the experimental

²⁰ S. Mizushima and K. Higasi, Proc. Imp. Acad. 8, 482 (1932).²¹ J. Y. Beach and K. J. Palmer, J. Chem. Phys. 6, 640 (1938); J. Y. Beach and A. Turkevich, J. Am. Chem. Soc. 61, 306 (1939).²² G. L. Lewis and C. P. Smyth, J. Chem. Phys. 7, 1085 (1939).²³ K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. 10, 428 (1942).²⁴ W. Altar, J. Chem. Phys. 3, 460 (1935).²⁵ W. D. Gwinn and K. S. Pitzer, J. Chem. Phys. 16, 303 (1948).

TABLE III. Interaction energies (kcal./mole) for 1,1,2-trichloroethane.

Interactions	$\phi=0^\circ$	30°	60°	90°	120°	150°	180°
Dipole-dipole	2.64	2.60	2.43	1.83	1.15	0.55	0.34
Exchange							
repulsions	16.09	17.42	19.19	17.53	15.78	16.16	16.70
van der Waals	-2.47	-2.97	-3.46	-2.60	-1.44	-0.85	-0.69
Induction	-0.71	-0.85	-1.00	-0.74	-0.42	-0.24	-0.20
Sum	15.55	16.20	17.16	16.02	15.07	15.62	16.15

results we have tried several sets of values of the parameters V_1 and V_3 , and have obtained the best results with values of 2000 and 200 cal./mole respectively. The calculated $\mu-T$ curve, using the potential function $V(\phi) = (2000/2)(1 + \cos\phi) + (200/2)(1 + \cos 3\phi)$, is shown in Fig. 1 (curve C-4), and it is evident that the agreement achieved is only slightly better than that obtained with the one-parameter function. This calculation was performed with the aid of charts in an article by W. J. Taylor,²⁶ written in connection with another problem, but making use of similar functions.

The one-parameter analysis fits 1,1,2-trichloroethane even less well, since it leads to a monotonic rise of dipole moment with temperature whereas the experimental curve shows a flat minimum, amounting to but a slight departure from constancy, so slight as possibly to be due to an abnormal experimental error, not evidenced but shortly to be checked. Figure 1 (curve C-2) shows a $\mu-T$ curve computed from Eqs. (2) and (3), and $V(\phi) = (2080/2)(1 + \cos\phi) + (1260/2)(1 + \cos 3\phi)$, the curves being made to match at 110°C . Taylor's charts were used to evaluate the integrals. It is clear that the results are as poor as with the one-parameter function. Several other attempts were made to adjust the parameters in functions of the type of Eq. (6), as well as the type $V(\phi) = (V_1/2)(1 + \cos\phi) + (V_3/2)(1 - \cos 3\phi)$, but not with good results. For example, evaluating graphically the integrals with $V(\phi) = (1100/2)(1 + \cos\phi) + (2100/2)(1 - \cos 3\phi)$ at $T = 383.2^\circ\text{K}$, and using $m(\text{CH}_2\text{Cl}) = 1.85$ and $m(\text{CHCl}_2) = 1.57$, one obtains $\mu = 1.89$, rather than the experimental value 1.45. This $V(\phi)$ was employed because it is an approximate algebraic expression of the potential energy *vs.* ϕ curve computed by intramolecular interactions as described below.

The moment variation of 1,1,2-trichloroethane is so slight that it might well be considered with those of the molecules in Table IV. The potential energy curve calculated by Turkevich and Beach²⁷ and found consistent with their electron diffraction results has been recalculated with the addition of the attractive energy due to the inductive effects of the permanent dipoles upon the polarizable atoms and the attractive energy due to dispersion interaction. The calculated interaction energies in Table III give a curve similar in general form to that of Turkevich and Beach.

²⁶ W. J. Taylor, J. Chem. Phys. **16**, 257 (1948).

²⁷ A. Turkevich and J. Y. Beach, J. Am. Chem. Soc. **61**, 3127 (1939).

TABLE IV. Molecules with temperature independent dipole moments.

	Temp. range, $^\circ\text{C}$	Dipole moment $\times 10^{18}$
1,1,2,2-tetrachloroethane*	128-163	1.36
1,3-dichloropropane*	101-201	2.07
1,4-dichlorobutane	160-235	2.22
1,3-dichloropropene		
104° isomer	124-205	1.79
112° isomer	122-230	1.81

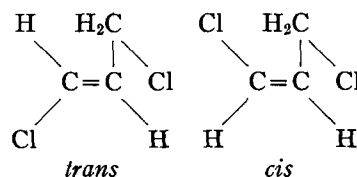
* See reference 10.

Quantitative calculations with these energies and also with a second set of values obtained by choosing 0.15 as the ratio of coulombic to exchange energy instead of 0.20 as in the first set of values fail to reproduce the moment values satisfactorily. Qualitatively, it appears that the explanation of the absence of any considerable variation of moment with temperature is similar to that offered previously¹⁰ in the case of 1,1,2,2-tetrachloroethane, namely, the inability of the molecules to pass in considerable numbers from potential minima corresponding to moderate moment values over high barriers to positions of higher energy and higher moment.

Molecules with Temperature Independent Dipole Moments

Table IV lists the molecules whose dipole moments might be expected to be temperature sensitive but which are found to be constant over the temperature range investigated. The reason for expecting a variation of moment with temperature is that for each molecule there is hindered rotation between two groups, each of which carries an unbalanced dipole. In general, if the experimental temperature range were great enough, a variation of dipole moment would be evident for each of the five molecules in the table. The only exception to this is the *trans*-isomer of 1,3-dichloropropene, as will be explained below. From a consideration of the interactions among the chlorines in 1,1,2,2-tetrachloroethane, Smyth and McAlpine¹⁰ have shown why it is reasonable to expect only a small increase in the dipole moment for this molecule in the short temperature range available.

The case of the isomers of 1,3-dichloropropene is interesting in that the measured vapor dipole moments do not serve to identify the isomers as the *cis*- or *trans*-stereoisomers. From a study of the Stuart models of these molecules one can see qualitatively why the two measured dipole moments should be so similar. In the *trans*



isomer the C—C axis of rotation is parallel to the fixed C—Cl vector. Hence one would expect a net dipole moment practically independent of temperature, whether or not the hindrance to the internal rotation be large, small, or varying strongly with azimuthal angle. If the value 1.44 is assigned to the moment of the C—Cl dipole adjacent to the double bond and 1.85 to the other C—Cl moment with an angle of 110° between the directions of the two dipole axes, a resultant moment 1.92 is calculated for the molecule. The discrepancy between this calculated value and the observed, 1.79 or 1.81, is less than the possible error resulting from uncertainties in the bond moment values. In the *cis*-molecule, a very large potential energy should exist in the position $\phi=0^\circ$ ($\phi=0^\circ$ when the two chlorines are in closest proximity), a minimum energy at 180° , and two shallow minima not far from $80-90^\circ$ and $270-280^\circ$. The positions of maximum moment, which are virtually excluded because of their high potential energies, lie not far from $\phi=0^\circ$, while the minimum moment, about 1.2×10^{-18} , should occur at $\phi=180^\circ$. The moment value corresponding to the two shallow minima is calculated to be about 2.5, if one neglects mutual inductive effects, which would lower the resultant moment somewhat. To push a considerable number of molecules to positions in the neighborhood of $\phi=0^\circ$ would require a temperature above that usable in the present measurements, while the variation in energy between the angles 80° and 280° is so small that a moderate change of temperature does not greatly alter the moment distribution. The absence of measurable moment variation in the rather limited temperature range obtainable is, therefore, not surprising, and the observed moment value, 1.79 or 1.81, is of the magnitude to be expected.

A factor which has not been considered in the discussion of the three unsaturated molecules is the possible introduction of some double bond character into the single carbon-carbon bond by resonance contributions arising from the presence of the double bond. Such double bond character would tend to introduce new potential barriers restricting rotation or alter the heights and locations of the barriers arising from steric and electrostatic effects. This would generally tend to reduce the variation of moment with temperature over the limited range experimentally attainable. In the *cis*-1,2-dichloropropene molecule, the near approach of the two chlorines for values of ϕ not far from zero would tend to stabilize the resonating structure with a positive chlorine and thus reduce the high moment of this configuration. Induction between the two adjacent C—Cl dipoles would also lower the moment of this configuration. Insofar as these positions were occupied to an appreciable extent, these two effects would tend further to reduce any increase of moment with rising temperature.

1,3-dichloropropane and 1,4-dichlorobutane have respectively two and three degrees of internal restricted rotation. If there were completely free internal rotation about each of the bonds, we would expect the significantly larger moments given μ_f in Table II. In view of the uncertainty in the assignment of group moments in these molecules, no great significance should be attached to the numerical discrepancy between the moment for free rotation μ_f and the experimental values. However, in going from the two-carbon to the three-carbon molecules having terminal polar groups, the discrepancy $\mu_f - \mu_{obs}$ decreases considerably. This is due to the decrease in polar group interaction caused by their greater average separation.^{17,28} In the 1,4-dichlorobutane we would expect much less interaction between the terminal C—Cl groups, since here they are separated by two methylene groups. Were there no other type of interaction then we would look for $\mu_f - \mu_{obs} = 0$ in the butane. Another interaction is that which occurs between the methylene groups in long paraffin chains. Taylor²⁶ has shown that, if one accepts the planar *trans*-configuration of three successive carbons in a paraffin chain as the most stable, as shown by x-ray analysis on crystalline normal paraffins, the existence of the restricted rotation at each C—C bond causes a greater contribution to the average configuration from the extended forms than would occur if there were completely free rotation. In 1,3-dichloropropane, this paraffin-like interaction may make itself felt and give greater prominence to the zig-zag configuration, for which the two C—Cl moments are on the same side of the chain. In 1,4-dichlorobutane, the paraffin-like interaction may well be the predominant one, but here the extended zig-zag configuration brings the C—Cl moments more into opposition. Consequently, the consideration of the paraffinic interactions alone would lead one to expect a larger $\mu_f - \mu_{obs}$ for the 4-carbon compound than for the 1,3-dichloropropane.

It will be noted that no quantitative account has been taken of variation of inductive effect with azimuthal angle. When change in azimuthal angle brings two C—Cl dipoles close together, their moments are lowered by mutual induction. Even when the two dipoles are far apart, the angle made by the axis of the resultant moment of the C—Cl dipole and its environment with the adjacent C—C bond is actually somewhat different from the assumed 110° and may change a little with change in azimuthal angle. The more important effect of lowering of moment by mutual induction cannot be calculated with accuracy. The effect would be partially compensated by the use of a somewhat lower moment value, which would incorrectly average the effect over the whole 360° variation of the azimuthal angle, but would give lower calculated potential barriers and moment variations, more nearly as observed.

²⁸ C. P. Smyth and W. S. Walls, *J. Chem. Phys.* **1**, 200 (1933).