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Induction Between Bond Moments in Some Halogenated Methanes

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The dipole moments of four fluorochloromethanes are measured in the vapor state. The inductive effects of carbon-halogen bond moments are calculated and, through these, the moments of methyl fluoride and methyl chloride are used to calculate approximate values for CH_2Cl_2 , CHCl_3 , and CFCl_3 , which are in satisfactory agreement

with the observed values. The moments of these molecules are then used to calculate values for other substituted methanes which are in excellent agreement with the observed values. The value of a bond moment is treated as a function of its environment.

IN an earlier paper¹ experimental determinations of the dipole moments of di- and tribromo- and iodomethanes were reported and the results were confirmed by the measurements of Müller and Sack.² In this first paper on the substituted methanes the moment of each molecule was treated as the resultant of the moments of dipoles lying in the lines joining the carbon and halogen nuclei. The observed moments were smaller than those calculated on the assumption that these bond moments did not affect one another and acted at an angle of 109.5° to one another, the normal carbon tetrahedral valence angle. Kinetic theory diameters were, therefore, calculated for the halogen atoms and assumed to cause widening of the valence angles, which were calculated from these diameters and from the carbon-halogen nuclear separations estimated from spectroscopic and x-ray data. The distance between the two chlorine nuclei in methylene chloride was calculated to be 3.00\AA , while Wierl³ later found from electron diffraction a distance of $3.16 \pm 0.06\text{\AA}$ in methylene chloride and $3.04 \pm 0.04\text{\AA}$ in chloroform. In methylene bromide, the distance between the bromine nuclei was calculated to be 3.20\AA , while Wierl found $3.35 \pm 0.04\text{\AA}$ in carbon tetrabromide, and, in methylene iodide, the distance between the iodine nuclei was calculated to be 3.62\AA , while Huggins and Noble,⁴ by means of x-ray analysis,

found 3.56\AA in crystalline iodoform and reported values 3.86 and $3.80 \pm 0.2\text{\AA}$ as found by Brockway and Pauling for iodoform in benzene solution. The angles between 120° and 135° obtained from these calculated distances gave calculated dipole moments in excellent agreement with the observed, an agreement which was termed somewhat fortuitous because of the speculative nature of the reasoning, uncertainties in some moment values, and neglect of the inductive effect of each dipole upon the rest of the molecule.

Smallwood and Herzfeld⁵ showed that this inductive effect could lower the moment of an ortho-disubstituted benzene from the value calculated as the resultant of two mutually independent dipoles acting at an angle of 60° to each other to the observed value, a not inconsiderable decrease. As the dipoles in the halogenated methanes are closer together than those in the ortho-disubstituted benzenes, it is evident that some attempt should be made to take account of their inductive effects.

Wierl's electron diffraction experiments give larger carbon-halogen distances than do Pauling's atomic radii⁶ and valence angles between 110° and 115° for the chlorinated methanes, not establishing the existence of any widening of the valence angle beyond the regular tetrahedral angle rounded off to 110° . In view of this, we shall examine the moments of chlorine-substituted methanes with 110° valence angles assumed between the bonds and shall tentatively make a

¹ C. P. Smyth and H. E. Rogers, *J. Am. Chem. Soc.* **52**, 2227 (1930).

² H. Müller and H. Sack, *Phys. Zeits.* **31**, 815 (1930).

³ R. Wierl, *Ann. d. Physik* [5] **8**, 521 (1931).

⁴ M. L. Huggins and B. A. Noble, *Am. Mineral.* **16**, 519 (1931).

⁵ H. M. Smallwood and K. F. Herzfeld, *J. Am. Chem. Soc.* **52**, 1919 (1930).

⁶ L. Pauling, *Proc. Nat. Acad. Sci.* **18**, 293 (1932).

similar assumption in the case of fluorine-substituted methanes, although calculation shows the possibility of a greater widening of the angle between two C—F bonds than that in the case of two C—Cl bonds.

The kindness of Dr. Albert L. Henne of Ohio State University has made it possible for us to measure four pure samples of methanes con-

taining both fluorine and chlorine substituents prepared by him.

EXPERIMENTAL RESULTS

The dielectric constants ϵ of the four vapors were measured with an apparatus and method described elsewhere. From each measurement of the dielectric constant, the polarization was

TABLE I. *Experimental data.*

$T(^{\circ}\text{K})$	CHFC_2Cl $p(\text{mm})$	P	$T(^{\circ}\text{K})$	CHF_2Cl $p(\text{mm})$	P	$T(^{\circ}\text{K})$	CFCl_3 $p(\text{mm})$	P	$T(^{\circ}\text{K})$	CF_2Cl_2 $p(\text{mm})$	P
304.7	426.3	51.36	303.9	971.5	55.95	299.2	586.6	29.00	304.7	738.7	25.93
	313.5	51.01		748.2	55.69		577.5	29.16		515.4	25.70
	246.0	50.85		579.4	55.50		541.3	29.23		471.0	25.58
	244.3	50.96		413.9	55.30		518.3	28.97		465.4	25.58
	227.6	50.83		273.0	55.06		424.4	28.71		459.8	25.76
	0	50.55		228.8	54.86		293.7	28.61		435.7	25.75
				157.7	54.73		261.6	28.62		354.4	25.60
305.8	388.6	51.12		0	54.75		250.2	28.49		162.3	25.76
	335.1	50.97					0	28.06		0	25.35
	329.4	50.98	311.0	679.5	54.69						
	283.4	50.92		674.3	54.66	304.3	499.5	28.69	311.1	730.0	25.68
	267.5	50.74		672.7	54.70		490.3	28.70		620.9	25.62
	231.2	51.00		467.4	54.46		436.6	28.72		520.9	25.59
	157.5	50.72		283.0	54.27		359.0	28.58		385.4	25.40
	0	50.55		219.6	53.90		277.3	28.27		0	25.20
				0	53.82		182.6	28.22			
340.0	467.5	47.63					180.7	28.20	348.8	680.6	24.94
	358.3	47.55	347.9	659.8	50.24		0	27.92		529.4	24.87
	344.1	47.45		526.6	50.05					509.1	24.80
	319.7	47.64		447.2	50.14	322.6	565.8	28.48		385.3	24.82
	247.0	47.16		283.1	49.69		545.3	28.46		325.1	24.80
	212.8	47.35		0	49.65		515.9	28.35		251.3	24.43
	184.1	46.80					515.7	28.42		0	24.67
	0	47.10	391.5	706.4	46.18		422.3	28.38			
				586.8	46.14		369.6	28.22	389.2	917.7	24.33
385.3	590.8	44.34		451.6	46.13		347.2	28.28		763.4	24.25
	494.4	44.18		400.7	45.91		290.5	28.12		633.5	24.34
	403.1	44.05		223.4	45.70		279.8	28.35		573.3	24.27
	382.5	44.08		0	45.80		272.9	28.19		413.2	24.19
	338.6	44.11					0	27.88		0	24.28
	329.1	44.08	433.0	760.0	43.23						
	295.8	44.00		602.9	43.17	342.6	529.1	28.08	421.2	914.6	23.98
	0	43.70		591.1	42.97		510.8	28.04		900.5	23.91
				532.4	42.99		456.0	27.95		780.1	23.86
424.3	639.6	41.95		469.4	43.28		366.1	27.82		722.5	23.89
	519.6	41.85		446.7	42.82		269.7	27.73		619.7	23.92
	474.1	41.74		0	42.80		261.6	27.72		0	23.91
	371.3	41.43					193.5	27.25			
	357.9	41.57	478.7	721.6	40.19		189.9	27.40	470.3	959.7	23.59
	0	41.14		651.0	40.30		186.9	27.44		926.2	23.67
				612.5	40.16		182.9	27.01		920.3	23.45
				546.9	40.49		0	27.40		848.4	23.56
				455.5	40.18					787.8	23.39
				446.9	40.25	375.9	568.2	27.61		785.8	23.39
				0	40.25		541.0	27.66		0	23.51
							455.6	27.56			
							360.6	27.48			
							350.7	27.78			
							264.9	27.45			
							257.4	27.53			
							256.8	27.27			
							0	27.23			

calculated as

$$P = [(\epsilon - 1)/(\epsilon + 2)]V, \quad (1)$$

where V is the molar volume. As the ideal gas law was used in calculating P , the dielectric constant was measured for several different pressures at each temperature and the calculated polarizations were extrapolated to zero pressure to obtain a value of the polarization free from error caused by deviations from the ideal gas law. It may easily be shown that, at these pressures, the polarization-pressure curve is practically a straight line with a slope proportional to the second virial coefficient of the gas. Extrapolation of the polarization to zero pressure is, therefore, a simple matter, although the accuracy of the polarization values is insufficient to give a satisfactory value for the second virial coefficient.

Table I gives the values of the polarization for the different pressures at each temperature on the absolute scale, the extrapolated values being given for zero pressure. These latter values were used to calculate for each substance the constants of the Debye equation,

$$P = a + b/T. \quad (2)$$

The value of the atomic polarization was calculated as $P_A = a - P_E$, the molar refraction for infinite wave-length, P_E , being obtained by

TABLE II. Constants of substituted methanes.

	a	P_E	P_A	b	$\times 10^{18}$
CH ₃ Cl ₂	17.0	16.1	0.9	10,260	1.29
CHF ₂ Cl	15.1	11.2	3.9	12,040	1.39 ₆
CFCl ₃	23.8	20.8	3.0	1,256	0.45
CF ₂ Cl ₂	20.1	16.0	4.1	1,600	0.51

TABLE III. Moments ($\times 10^{18}$) of substituted methanes.

CH ₃ F ^a	1.80 ₃	CCl ₄	0 ^b	CH ₃ Cl	1.85 ^b
CH ₂ Cl ₂	1.29	CF ₂ Cl ₂	0.51	CH ₂ Cl ₂	1.57 ^a
CHF ₂ Cl	1.39 ₆	CFCl ₃	0.45	CHCl ₃	1.05 ^b

^a Measurement in this laboratory to be published shortly.

^b Smyth, *Dielectric Constant and Molecular Structure*, Appendix I, New York, The Chemical Catalog Co. Inc., 1931.

^c K. L. Wolf and O. Fuchs, *Stereochemie* (K. Freudenberg), p. 244, Leipzig, Franz Deuticke, 1932.

extrapolation from the sums of atomic refractions or of electron group refractions for the sodium D line.⁷ The dipole moments were calculated from the values of b as $\mu = 0.01273 \times 10^{-18}(b^{1/2})$ and should be in error by no more than 0.01×10^{-18} . The values of these constants are given in Table II, while Table III lists the moments together with those of other molecules needed for the discussion of the results.

DISCUSSION OF RESULTS

In view of the very small difference, 0.04×10^{-18} , between the moment of methyl fluoride and that of methyl chloride, the not inconsiderable moments of CF₂Cl₂ and CFCl₃ and the marked increase in moment caused by replacement of chlorine in CHCl₃ by fluorine show that the effects of induction and of the widening of valence angles by repulsion must be considered. The zero moments recently reported by van Arkel and Snoek⁸ for the moments of CFBr₃ and CCl₃Br in benzene solution may be attributed to the fact that moments as small as these should be cannot be accurately determined by measurements on liquids.⁹ Although it was possible to explain the moments of CH₂Cl₂ and CHCl₃ as the resultants of moments in the C-Cl bonds, the angles between which were widened beyond 110° by mutual repulsion of the chlorines, an analogous explanation of the fluorochloromethane moments is possible only if the fluorine atoms give rise to a much smaller mutual repulsion than that between the chlorines. As a rough calculation of the internuclear distances in methylene fluoride carried out in the same way as those for the other methylene halides indicated a greater repulsion than in the case of the chloride, it would appear that the explanation is to be sought primarily in the inductive effects. This is in accord with the approach to the problem announced at the beginning of the paper because of the closeness of the valence angles of the chloromethanes to 110° found by Wierl and

⁷ Landolt-Börnstein, 5th edition, p. 985. Smyth, *Dielectric Constant and Molecular Structure*, p. 153, New York, The Chemical Catalog Co. Inc., 1931.

⁸ A. E. van Arkel and J. L. Snoek, *Zeits. f. physik. Chemie [B]* **18**, 159 (1932).

⁹ Smyth, *Dielectric Constant and Molecular Structure*, p. 168, New York, The Chemical Catalog Co. Inc., 1931.

because of the considerable inductive effects calculated by Smallwood and Herzfeld for the ortho-disubstituted benzenes.

The polarizability α of a portion of a molecule may, as a rough approximation, be treated as if the polarization occurred at one point. The moment induced at this point by a permanent moment m elsewhere in the molecule can then be calculated by the method of Smallwood and Herzfeld. If the dipole m exerting the force E is located at the origin of a set of plane polar coordinates, the horizontal and vertical components of E (E_x and E_y) at the point r , where the polarizability acts, are given by

$$\begin{aligned} E_x &= m_x(3 \cos^2 \theta - 1)/r^3 + 3m_y(\sin \theta \cos \theta)/r^3 \\ E_y &= 3m_x(\sin \theta \cos \theta)/r^3 + m_y(3 \sin^2 \theta - 1)/r^3 \end{aligned} \quad (3)$$

where m_x and m_y are the components of m , which lies in the x, y plane. The moment induced by m at the point r has the components

$$m_{ix} = E_x \alpha \quad \text{and} \quad m_{iy} = E_y \alpha. \quad (4)$$

The treatment of the effect of a system of charges as being that of a single dipole located at a point within the system becomes an extremely rough approximation when the effect is considered at distances as small as those involved in the halogenated methanes. Although it is certainly justifiable to treat the principal dipole of CH_3Cl as lying in the $\text{C}-\text{Cl}$ line, its size and its location in this line are uncertain. In the case of the dihalogenated benzenes, Smallwood and Herzfeld found it necessary to locate the dipoles arbitrarily at the circumference of the carbon atoms to which the particular groups were attached. Consideration of the locations of the centers of gravity of the charges assignable to the $\text{C}-\text{Cl}$ portion of the molecule places the principal dipole 7/8 of the distance, 1.76Å,⁶ from the carbon nucleus to the chlorine nucleus.¹⁰ A moment m located at this point would induce a moment in each of the three $\text{C}-\text{H}$ bonds, which is calculated in terms of m by using Eqs. (3) and (4), the arbitrary assumption being made that a polarizability, $\alpha = 0.66 \times 10^{-24},^{5,11}$ acts at the midpoint of the $\text{C}-\text{H}$ bond, 0.53Å from the carbon nucleus. If the presumably small and

unknown moment of the $\text{C}-\text{H}$ bond is neglected, the observed moment, 1.85×10^{-18} , may be regarded as the sum of m and the components of the three induced $\text{C}-\text{H}$ moments along the projection of the $\text{Cl}-\text{C}$ line. m is thus calculated as 1.15×10^{-18} and the moment induced by it in each $\text{C}-\text{H}$ as 0.70×10^{-18} . This value 1.15×10^{-18} is, however, too high for the permanent moment of the $\text{C}-\text{Cl}$ bond as no account has been taken of the inductive effect of the $\text{C}-\text{H}$ moments, 0.70×10^{-18} , back upon the $\text{C}-\text{Cl}$. This effect may be calculated and a still smaller value may be used for the $\text{C}-\text{Cl}$ moment, the moments induced in the $\text{C}-\text{H}$ bonds being taken into account in all subsequent calculations. However, in view of our ignorance of the moment of the $\text{C}-\text{H}$ bond arising from possible inherent electrical unsymmetry and of other uncertainties which cannot be eliminated from the treatment, it appears rational, in cases where at least one hydrogen is attached to the carbon, to assign the entire moment of the methyl halide to the carbon-halogen bond. The results of such treatment will not differ greatly from those to be obtained by using a smaller carbon-halogen bond moment and adding the effects of the $\text{C}-\text{H}$ bonds.

In the methylene chloride molecule two moments of 1.85×10^{-18} each in the $\text{C}-\text{Cl}$ lines at an angle of 110° to one another would have a resultant, 2.13×10^{-18} , as compared to the observed value, 1.57×10^{-18} . With the dipoles located 7/8 of the distance from the carbon to the chlorine nucleus, that is, 1.54Å from the carbon nucleus, and polarizabilities, $\alpha = 2.51 \times 10^{-24},^{5,11}$ assumed to be acting at the same points,—a reasonable assumption,—application of our equations shows that the inductive effect of one moment of 1.85 lowers the moment in the other $\text{C}-\text{Cl}$ line to 1.36. The resultant of two such moments happens to be identical with the observed moment of methylene chloride. However, the moment of 1.36 would have a smaller inductive effect and the lowering calculated for the other $\text{C}-\text{Cl}$ moment would not be as great. This, in turn, would have a smaller inductive effect upon the first moment. Successive calculations lead to a value 1.49 for the moment of a $\text{C}-\text{Cl}$ bond when a second chlorine is attached to the same carbon. This would give a moment of

¹⁰ Cf. L. Meyer, *Zeits. f. physik. Chemie* [B] 8, 27 (1930).

¹¹ Smyth, *Phil. Mag.* 50, 361 (1925).

1.71 for methylene chloride if the two C—Cl moments acted at an angle of 110° to each other, but the induced moments do not lie in the C—Cl lines, so that the resultant C—Cl moments make a slightly smaller angle with each other and have a resultant of 1.79, which is 0.22 higher than the observed value for methylene chloride.

Since one C—Cl dipole lowers the moment of another from 1.85 to 1.49, one might, as a very rough approximation, assume that two C—Cl dipoles would produce a lowering of 2×0.36 in a third C—Cl moment. In chloroform, which has a moment $\approx 3(\text{C—Cl}) \cos 70^\circ = (\text{C—Cl})$, the moment would, therefore, be 1.13 as compared to an observed value, 1.05. A more accurate treatment involving the calculation of the components along three reference axes leads to a value of approximately 1.35. Obviously, if the assumed location of the permanent dipole is moved in toward the carbon nucleus, the inductive effect will be increased. Thus, with the dipoles and the polarizabilities located $2/3$ of the distance from the carbon to the chlorine nucleus instead of $7/8$, still much farther from the carbon than assumed by Smallwood and Herzfeld, a C—Cl moment of 1.85 reduces the other C—Cl to 1.03 instead of 1.36 as in the previous case. Although better agreement between the calculated and the observed values of the moments would result from this moving in of the dipoles, such agreement would not be justified by the nature of the treatment. It, therefore, seems better to adhere to the original assumption as to the dipole location, an assumption which is theoretically plausible. Similar calculations show that because of its much smaller polarizability, $\alpha = 0.626 \times 10^{-24}$, the C—F moment is less reduced by the inductive effect of an adjacent C—Cl than is a C—Cl moment, and because of the smaller C—F distance, 1.41Å, the C—F moment reduces an adjacent C—Cl moment more than another C—Cl moment does. Table IV gives the lowering of one carbon-halogen bond moment by the inductive effect of another on the same carbon.

The reason for the not inconsiderable moment

TABLE IV. Lowering of carbon-halogen moment ($\times 10^{18}$).

C—Cl by C—Cl	0.36	C—F by C—Cl	0.11
C—Cl by C—F	0.56	C—F by C—F	0.21

of CFCl_3 is apparent in the marked differences in the moment lowerings in Table IV. The components in the F—C line of the moments induced by the C—F in the three C—Cl's are so large as to cancel a large fraction of the components of the permanent moments in this line, while the C—F moment is less affected by the three C—Cl's. The resultant difference calculated, 1.2, is much larger than the observed moment, 0.45. It is probable that the methyl halide moments assigned to the carbon-halogen bonds include so much of the H—C bond moment, at least, part induced, and, perhaps, part permanent, that they are considerably too high for use when no hydrogen is attached to the carbon. The calculation of the moments induced in the H—C's in methyl chloride gave a moment of 1.15 for the C—Cl and a similar calculation for methyl fluoride gives 0.91 for the C—F, the effects of the induced H—C moments upon the halogens being disregarded in the calculation. As this neglected effect raises the apparent values for the carbon-halogen bond moments, these may reasonably be rounded off to about 1.0 for C—Cl and 0.8 for C—F. A more accurate calculation of these values is impossible because of their great dependence upon the unknown location of the point at which the polarizability of the H—C bond may be supposed to act. The use of these values in the calculation of the CFCl_3 moment gives, instead of 1.2, a value of 0.44 as compared to the observed 0.45.

These lower carbon-halogen bond moments may be used equally well in calculating the moments of CH_2Cl_2 , CHCl_3 , etc., because their inductive effects upon the H—C bonds bring the total resultant moments up to the same magnitude as those obtained by using methyl halide moments for the bond moments. It is somewhat disconcerting, at first, to find the use of these much smaller bond moments necessary in some cases, but consideration of the nature of a bond moment makes it clear that its apparent value cannot be constant under all conditions. The system of charges constituting a carbon-halogen group cannot be isolated from the rest of the molecule, and, unless we could determine exactly a point in the system where its moment could be regarded as acting and, similarly, a location for its polarizability, nothing would be gained by

this process of isolation. A bond moment is merely a measure of the electrical unsymmetry of a certain section of a molecule and is affected by the environment of the section. If the immediate environment of the section in different molecules is the same, the bond moment remains constant; if it is different, the electrical unsymmetry of the section and its moment changes. For example, we may think of the carbon tetrachloride molecule as resolved into four equal C—Cl moments, which, because of the symmetry of the molecule, cancel one another to give zero resultant moment. Each C—Cl moment consists of the moment due to an inherent unsymmetry in the distribution of charge plus the moments induced by each of the three other C—Cl moments. In methyl chloride, the C—Cl moment contains the components in the C—Cl line of the moments induced by the H—C moments, which consist of a possible permanent moment plus the moment induced by the C—Cl moment. As only the roughest kind of separation of these effects can be made, it is as well to treat the entire moment of the molecule as the C—Cl moment. Attachment of more carbons to the methyl carbon gives molecules of somewhat increased moment because of induction,¹ but the effect is noticeable through only two carbons of a chain. Little error will arise from treating the moment of the —CH₂Cl group as a C—Cl moment equal to that of methyl chloride. In chlorobenzene, the immediate environment of the C—Cl is different from that in an alkyl chloride and the moment is somewhat different. If two C—Cl's are separated from one another as in *p*- or *m*-dichlorobenzene, the moment of chlorobenzene may, with little error, be used as a C—Cl bond moment to calculate the resultant moment of the disubstituted molecule. However, in *o*-dichlorobenzene, each C—Cl bond moment is affected by the proximity of the other, not only through direct inductive effects of one C—Cl upon the other, but also through the effects upon the other adjacent parts of the molecule. The very approximate calculation by Smallwood and Herzfeld of the alteration in moment produced by these effects was possible because it was not large. From a practical point of view, the most useful procedure is to assign to one bond the moment of an entire simple molecule containing but one polar group, but it must be born in mind

that, when the immediate environment of a bond moment changes, the moment may change.

The moment of CFCℓ₃, which has been calculated in our previous discussion, makes an excellent starting point for the consideration of the moments in Table III. In the following equations, the formula of a molecule or of a bond enclosed in parentheses will represent its moment. The different bond moments are exposed to somewhat different inductive effects in the different molecules, but, as the total resultant moments of the molecules are not large, it is evident that the differences in inductive effects, which, in most cases, partially cancel one another, may commonly, as an approximation, be neglected. Since, however, the C—F bond in methyl fluoride is not exposed to the inductive action of other carbon-halogen bonds, one would expect the values calculated by Eqs. (12) and (14) to be lower than the moment of methyl fluoride. The moment of CFCℓ₃ lies in the C—F line and is given by

$$\begin{aligned}(\text{CFCℓ}_3) &= (\text{C—F}) - 3(\text{C—Cl}) \cos 70^\circ \\ &= (\text{C—F}) - (\text{C—Cl}) = 0.45, \quad (5)\end{aligned}$$

since $\cos 70^\circ = 1/3$. The moment of CF₂Cl₂ must lie in the line which bisects the F—C—F angle and also the Cl—C—Cl angle and is given by

$$\begin{aligned}(\text{CF}_2\text{Cl}_2) &= 2(\text{C—F}) \cos 55^\circ - 2(\text{C—Cl}) \cos 55^\circ \\ &= 1.15[(\text{C—F}) - (\text{C—Cl})]. \quad (6)\end{aligned}$$

Substituting for $[(\text{C—F}) - (\text{C—Cl})]$ its value given by Eq. (5),

$$(\text{CF}_2\text{Cl}_2) = 1.15 \times 0.45 = 0.52, \quad (7)$$

as compared to an observed value 0.51.

As an approximation, the moment of CHFCl₂ may be regarded as lying in the H—C line. Consequently,

$$\begin{aligned}(\text{CHFCl}_2) &= (\text{H—C}) \\ &\quad + (1/3)[(\text{C—F}) + 2(\text{C—Cl})]. \quad (8)\end{aligned}$$

A similar approximation gives

$$\begin{aligned}(\text{CF}_2\text{Cl}_2) &= (\text{C—F}) \\ &\quad - (1/3)[(\text{C—F}) + 2(\text{C—Cl})]. \quad (9)\end{aligned}$$

Adding (8) and (9),

$$(\text{CHFCl}_2) + (\text{CF}_2\text{Cl}_2) = (\text{H—C}) + (\text{C—F}), \quad (10)$$

but

$$(H-C) + (C-F) = (CH_3F) = 1.81 \text{ (obs.)}, \quad (11)$$

and

$$(CHFCl_2) + (CF_2Cl_2) = 1.29 \text{ (obs.)} \\ + 0.51 \text{ (obs.)} = 1.80. \quad (12)$$

The excellence of the agreement between the values calculated by (11) and (12) is accidental as is shown by a similar calculation involving chloroform.

$$(CHCl_3) = (H-C) + (C-Cl) = 1.05 \text{ (obs.)}. \quad (13)$$

Adding (5) and (13),

$$(CFCl_3) + (CHCl_3) = (H-C) + (C-F), \quad (14)$$

or $0.45 \text{ (obs.)} + 1.05 \text{ (obs.)} = 1.50$, while (11) gives $(H-C) + (C-F) = 1.81$. Subtracting (13) from (8) and rearranging,

$$(CHFCl_2) = (CHCl_3) \\ + (1/3)[(C-F) - (C-Cl)], \quad (15)$$

but $(CHCl_3) = 1.05$ and, from (5), $(1/3)[(C-F) - (C-Cl)] = 0.15$, consequently,

$$(CHFCl_2) = 1.05 + 0.15 = 1.20, \quad (16)$$

as compared to the observed value, 1.29.

As an approximation similar to that in (8),

$$(CHF_2Cl) = (H-C) \\ + (1/3)[2(C-F) + (C-Cl)]. \quad (17)$$

Subtracting (13) from (17) and rearranging,

$$(CHF_2Cl) = (CHCl_3) \\ + (2/3)[(C-F) - (C-Cl)], \quad (18)$$

but $(CHCl_3) = 1.05$ and, from (5), $(2/3)[(C-F) - (C-Cl)] = 0.30$, consequently,

$$(CHFCl_2) = 1.05 + 0.30 = 1.35, \quad (19)$$

as compared to the observed value, 1.40.

Although the $H-C$ moment cancels in the final calculations with all of these equations, it has been left in the initial equations to make clearer the assumptions. It is evident that the variation of moment among these different fluorochloromethanes agrees extremely well with the predictions of theory. The agreement between the observed moments and those calculated on the assumption of 110° carbon valence angles does not preclude the possibility of widening of the angles in, at least, some of the methanes. Indeed, it seems probable that there is more or less widening of the angles in all of the unsymmetrically substituted methanes, although, in some cases, this may be too small for detection by means of x-ray or electron diffraction. It would appear, however, that induction is much more important than angle widening in determining the moments of the methanes considered in this paper.

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