222. *The Dipole Moments of Vapours. Part VII. Calculation of Valency Angles in Chloroform and Methylene Chloride.*

By L. G. Groves.

On the basis of values for the moments of the C–Cl and the C–H link obtained from the moment of methyl chloride, it is shown, after allowances are made for components of induction, that the Cl–C–Cl intercovalency angle is approximately tetrahedral in both chloroform and methylene chloride. This result is in accord with the electron-diffraction results of Sutton and Brockway (*J. Amer. Chem. Soc.*, 1935, **57**, 473).

It has been shown in Part VI (J., 1937, 1992) that the total moment of a molecule not exhibiting resonance is made up of two parts, one of which is the parent moment or moments and the other the component due to induction caused by the proximity of the bond moment to polarisable portions of the molecule. Equations were derived enabling the latter quantity to be calculated with a fair degree of accuracy, and the values of the induced moment so obtained were, in many cases, found to be quite large.

In view of the fact that two conflicting sets of data are in existence for the carbon–chlorine intercovalency angles in chloroform and methylene chloride, it is of interest to calculate from the observed moment of methyl chloride and the various angles recorded, all the possible values of the moments of these two compounds.

Bewilogua (*Physikal. Z.*, 1931, **32**, 265), from *X*-ray measurements, obtained for the Cl–C–Cl angle θ, 124° ± 6° and 116° ± 3° in methylene chloride and chloroform respectively; Sutton and Brockway (*loc. cit.*) on the other hand, from electron-diffraction data, obtained a value of 111° ± 2° in both compounds.

In seeking to calculate the induced moment in neighbouring chlorine atoms due to any one C–Cl link, from the value of μ_{CH_3Cl}, some definite allowance must be made for the moment of the C–H bond. Owing to the tetrahedral structure of methyl chloride, the total moment is equivalent electrically to the sum of μ_{C-H} and μ_{C-Cl} acting along the same straight line, and in consequence, values of μ_{C-Cl} are obtained from μ_{CH_3Cl} by subtracting arbitrary values assigned to $\mu_{\mathrm{C-H}}$. In the ensuing calculations, $\mu_{\mathrm{C-H}}$ will be given the values 0, 0·15, and 0·20 D., which in conjunction with $\mu_{\mathrm{CH_3Cl}} = 1{\cdot}87$ (Groves and Sugden, J., 1937, 159) lead to 1·87, 1·72, and 1·67 respectively for $\mu_{\mathrm{C-Cl}}$. The method of obtaining the magnitude and direction of the induced components was described in detail in Part VI (*loc. cit.*), and the individual calculations will be omitted here.

In methylene chloride, each C–Cl moment induces moments in the neighbouring chlorine atoms, the resultant of which opposes the primary C–Cl dipoles, such that the total moment of the molecule is

$$2\mu_{\mathrm{C-Cl}} \cos \tfrac{1}{2}\theta - 2\mu_{\mathrm{ind.}} \cos \phi + 2\mu_{\mathrm{C-H}} \cos \tfrac{1}{2}\tau,$$

where ϕ = angle between the direction of $\mu_{\mathrm{ind.}}$ and the bisector of θ, and τ = tetrahedral angle.

The scheme of moments in chloroform is more complicated, as each C–Cl link induces moments in the remaining two chlorine atoms such that six induced components arise symmetrically disposed in pairs about the bisectors of θ. Thus the total moment

$$\mu_{\mathrm{CHCl_3}} = 3\mu_{\mathrm{C-Cl}} \cos \alpha - 6\mu_{\mathrm{ind.}} \cos \phi \,.\, \cos \beta + \mu_{\mathrm{C-H}}$$

where α and β are respectively the angles made by the C–Cl link and by the bisector of θ, with the median of the CCl_3 pyramid.

In these calculations the moments induced in the chlorine atoms by the C–Cl dipoles are alone considered; those similarly induced, but by the C–H dipole, are small enough to be neglected (maximum resultant value in chloroform = 0·01 D.).

The various results are set out below.

θ.	$\mu_{\mathrm{ind.}}/\mu_{\mathrm{C-Cl}}$.	$\mu_{\mathrm{C-Cl}}$.	$\mu_{\mathrm{C-H}}$.	ϕ.	α.	β.	Total moment.
			Methylene chloride.				
111°	0·224	1·87	0	40·4°	—	—	1·48
		1·72	0·15				1·53
		1·67	0·20				**1·55**
124	0·206	1·87	0	50·9	—	—	1·27
		1·67	0·20				1·37
			Chloroform.				
111	0·224	1·87	0	40·4	70·5°	57·1°	0·83
		1·72	0·15				0·92
		1·67	0·20				**0·95**
116	0·208	1·87	0	44·8	78·3	67·4	0·50
		1·67	0·20				0·65

The observed moments of methylene chloride and chloroform in the vapour state are respectively 1·59 D. and 0·95 D. (Sänger, *Physikal Z.*, 1926, **27**, 556), and inspection of the last column above shows that these values are most closely approached when Sutton and Brockway's values for θ (*i.e.*, approximately tetrahedral values) are chosen.

I wish to thank Prof. S. Sugden, F.R.S., for his interest in this work, and Dr. J. J. Fox, C.B., for permission to publish it.

GOVERNMENT LABORATORY, LONDON.

[*Received, May 3rd,* 1938.]