## Determination of Dipole Moment

There are a number of methods for ascertaining the dipole moment. We shall discuss the principle involved in a few of these.

(1) **Temperature Method**: From a direct measurement of the dielectric constant, the total polarisation ($P_t$) of a substance is obtained, M and p being separately determined. From eqn. 10.

$$P_t = A + B/T$$

If total polarisation $P_1$ and $P_2$ at two temperatures $T_1$ and $T_2$ then

$B = (P_1 - P_2)(T_1T_2 / T_2 - T_1)$

The value of the dipole moment μ is easily calculated from that of B, for,

$$B = 4\pi N \mu^2/9k$$

$$\text{or} \quad \mu = \sqrt{9kB/4\pi N} = 0.0128\times10^{-18}.\sqrt{B} \quad \text{.......................................} (12)$$

putting the standard values of N, k and π.

(ii) Ebert's Method. Polar molecules in gaseous state, if subjected to an electric field, will suffer both orientation as well as distortion polarisation. But if the same substance in solid state be subjected to the field, orientation of molecules is not possible and only distortion polarisation will occur. As such, for total molar polarisation,

$$P_{gas} = P_i + P_0; \qquad P_{solid} = P_i$$

Hence orientation polarisation, $P_0 = P_{gas} - P_{solid}$

$$\text{or} \quad 4\pi N \mu^2/9kT = P_{gas} - P_{solid}$$

$$\mu = \sqrt{\frac{9kT}{4\pi N}(P_{gas} - P_{solid})} \quad \text{..................................} (13)$$

Since the quantities on right-hand side are known, the value of μ is obtained.

## Dipole moment and Structure of Molecules

Dipole moment has proved a valuable weapon in our attack of structural problems of molecules. Its interpretation often leads to surprisingly important information about configuration of molecules.

Carbon dioxide has been found to be non-polar, $\mu=0$. With carbon atom in the middle, this triatomic molecule may either have the triangular structure (1) or the linear structure (II) as in

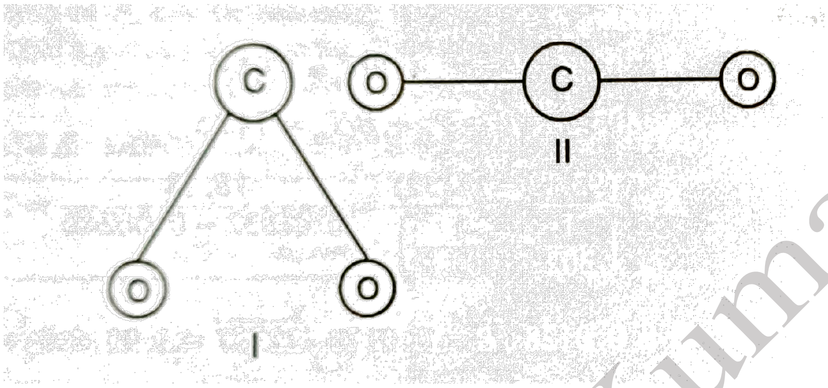

**Fig. 5**

Fig. 5 Since the electrons are drawn towards oxygen atoms, the triangular structure would always make the resultant molecule polar, whereas in the linear structure, the electric moment on one side of the carbon atom is counterbalanced by the moment on the opposite, so that the molecule would be non-polar. Hence, carbon dioxide molecule has a linear structure.

On the other hand, the water molecule has an appreciably large dipole moment, which rules out the possibility of its having a symmetrical linear structure. The molecule has a triangular structure, the two OH bonds, meeting at an angle. The electric moment created in one O-H bond does not neutralise that produced by the other.

The non-polar character of molecules like $H_2$, $Cl_2$, $N_2$, etc. point to the fact that the bonding electrons are symmetrically placed between the two atoms.. In fact, in all non-polar molecules there should be a complete symmetrical distribution of the positive and negative charges. The molecule must have an electrical centre of symmetry.

Thus, we find benzene as a non-polar molecule, which confirms the Kekule structure and that it has a planar configuration with its six hydrogen atoms in the same plane. If a part of the hexagon or if the hydrogen atoms were not in the same plane, it is easy to see that the molecule would have been polar.

Similarly, boron trichloride is non-polar which suggests that it has a planar configuration with three chlorine atoms at the corners of an equilateral triangle and boron at the intersection of medians. But $PCl_3$, or $NH_3$ molecules have dipole moments. In these molecules, the three halogen or hydrogen atoms are in one plane symmetrically placed in relation to the nitrogen (or phosphorus) atom placed at the apex of a regular pyramid.

Chemical bonding between two atoms is necessarily associated with an electrical moment arising out of the difference in electronegativity of the two atoms. This means that every bond carries with it an electrical moment called the 'bond moment'. The dipole moment of a molecule is really the vectorial sum of the individual bond moments present in it. To compute the dipole moment then it is necessary to find out the values of various bond moments, such as C-H, O-H, C-Cl etc. No direct method is known to obtain the magnitude of a bond moment. Though not based on a very satisfactory method, the bond moment of a C-H bond has been taken as 0.4 d. On this basis analysing the dipole moments of a large number of compounds, Eucken and Meyer prepared a table of moments for different bonds, such as,

| **H-C** | **C-Cl** | **CO** | **CO** | **H-0** | **H-N** |
|---|---|---|---|---|---|
| **04** | 1.5 | 0.7 | 2.3 | 1.6 | 1.3 |

The bond is directed towards the more electronegative of the two atoms linked.

All saturated hydrocarbons, $CH_4$ $C_2H_6$ , $C_3H_8$, etc. are found to be non-polar. Let us consider the simplest molecule, methane. Its non-polar character is easily understood from its symmetrical tetrahedral structure with the C-atom at the centre and the four identical valences making an angle of 109°28' with each other. The centre of symmetry is at the nucleus of the C-atom. The absence of dipole moment in the methane molecule implies that any one C-H bond moment exactly counterbalances the net moment contributed (vectorially) by the remaining three C-H bonds i.e., the methyl group as a whole. The $CH_3$ group has a regular pyramidal configuration with C-atom at its apex and three hydrogen at the base (**Fig. 6**). The resultant moment of the three C-H bonds will be directed along a line from the centre of the base towards the apex and opposite to the fourth C-H bond moment direction. Using symbol m for bond moments, the resultant moment of the $CH_3$ is given by

$$m_{CH3} = 3m_{CH}\,\mathrm{Cos}(180°' - 109°28') = 3m_{CH}\ x 1/3 = m_{CH}$$

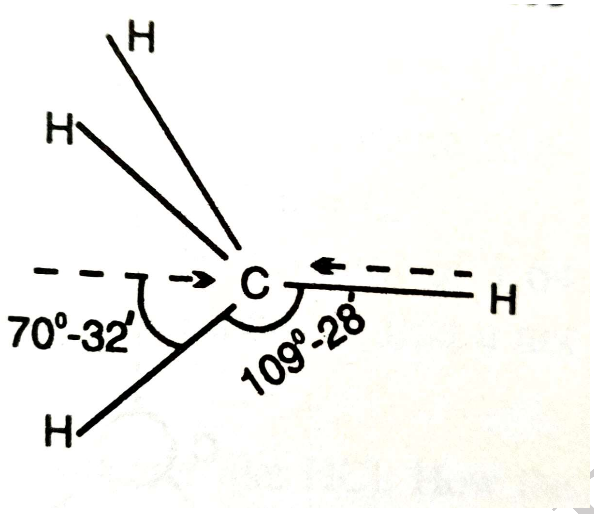

Fig. 6

That is, the moment of $CH_3$-group is the same as C-H bond, i.e., 0.4d. It is obvious that for identical reasons the moment of $C_2H_5$ or other alkyl groups will also be equal to a C-H bond moment.

Not only alkyl groups, other groups or radicals such as $NH_2$, $NO_2$, OH, etc. have definite moments, called group moments. These group moments would naturally depend upon the nature of linkages present in those groups. When one or more of such radicals are present in a molecule, these contribute towards the dipole moment of the same.

It leads to the conclusion that if a hydrogen atom in different saturated hydrocarbons be replaced by OH to produce homologous alcohols, all of the latter should have the same dipole moment. Similarly, all alkyl amines or alkyl chlorides would be expected to have identical dipole moment. This is borne out from experimental observations as shown in the table below.

**TABLE: DIPOLE MOMENTS (d)**

| **alkyl group** | **alcohols** | **amines** | **chlorides** | **nitriles** |
|---|---|---|---|---|
| **ethyl** | 1.70 | 1.3 | 2.04 | 3.57 |
| **propyl** | 1.66 | 1.4 | 2.04 | 3.57 |
| **Butyl** | 1.65 | 1.3 | 2.04 | 3.57 |

The magnitude of the group moments varies slightly in aromatic compounds from those in aliphatic ones. In 1929 Williams computed the following group moments for aromatic compounds:

| $NO_2$ | CHO | OH | Cl | Br | COOH | $CH_3$ | $NH_2$ | H |
|---|---|---|---|---|---|---|---|---|
| **-3.9** | -2.8 | -1.7 | -1.5 | -1.5 | -0.9 | +0.4 | +1.5 | 0.0 |

[-minus sign indicates the moment directed away from the aromatic ring.]

The measured dipole moment of water is 1.84 d and it results from two identical OH bonds each of moment 1.6d. The resultant as shown in Fig.7 works out to an angle of 105° between the two bonds. This illustrates the application of bond moments and also shows how the dipole moment enables us to determine the bond angles and hence the structure.

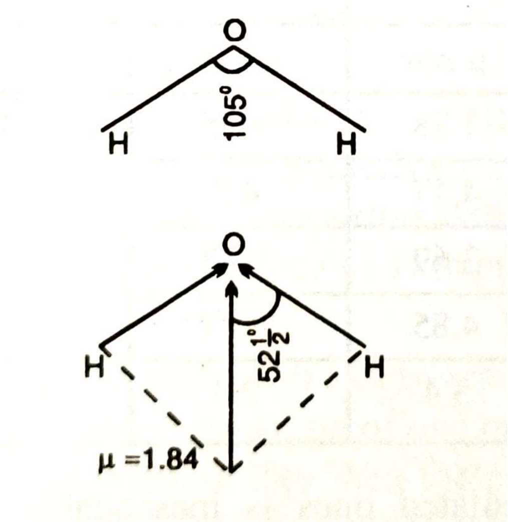

Fig. 7

Let us take another example. The structure of methyl alcohol is shown in Fig. 8, in which the known valence angles have been adopted. The bond moments are $m_{OH}$ =1.6, $m_{C\text{-}O}$=0.7, $mCH_3$ =$m_{CH}$ = 0.4 The resultant dipole moment comes 1.56 d while observed value is 1.65 d, thus conforming to the structure used in calculation.

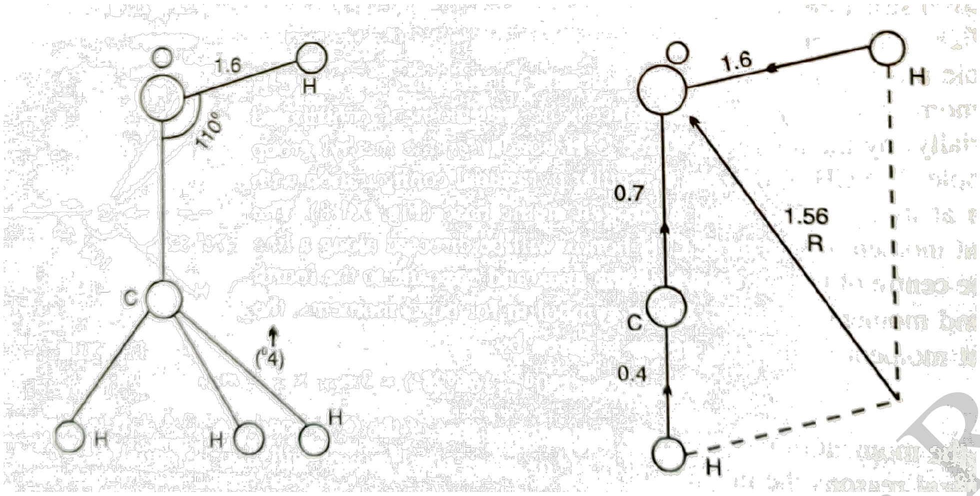

**Fig. 8**

Benzene, which is non-polar, acquires dipole-moment when one of its hydrogen is substitued. Thus, we have,

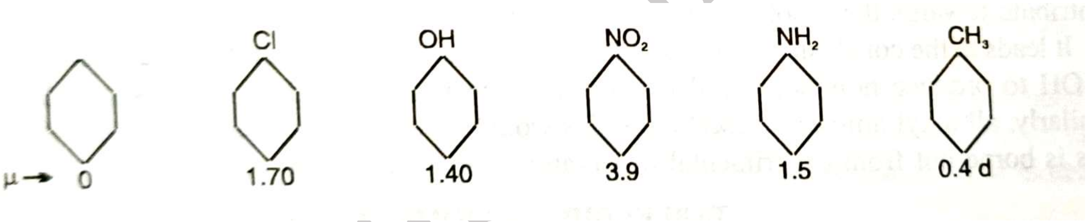

**Fig. 9**

That the vector sums of individual bond or group moments lead to the dipole moment is amply illustrated from a comparison of the calculated and measured dipole moments of many di-substituted benzene derivatives. If $m_1$ and $m_2$ be the bond moments and α be the angle between their directions for two substituents of benzene, then

$$\mu = \left[m_1^2 + m_2^2 + 2m_1m_2\cos\alpha\right]^{\frac{1}{2}}$$

It is easily seen that α = 60° for ortho, 120° for meta and for 180° for para derivatives.

The values for some of these compounds are tabulated here.

**TABLE: DIPOLE MOMENTS OF $C_6H_4X_1X_2$, COMPOUNDS**

| | | **ortho** | | **meta** | | **para** | |
|---|---|---|---|---|---|---|---|
| **$X_1$** | **$X_2$** | $\mu_{calc}$ | $\mu_{obs}$ | $\mu_{calc}$ | $\mu_{obs}$ | $\mu_{calc}$ | $\mu_{obs}$ |
| **$CH_3$** | Cl | 1.39 | 1.35 | 1.79 | 1.78 | 1.95 | 1.90 |
| **$CH_3$** | $NO_2$ | 3.76 | 3.66 | 4.16 | 4.17 | 4.3 | 4.4 |
| **Cl** | $NO_2$ | 5.26 | 4.60 | 3.68 | 3.69 | 2.52 | 2.7 |
| **$NH_2$** | $NO_2$ | 3.64 | 4.26 | 4.74 | 4.85 | 5.17 | 5.21 |
| **Cl** | CN | 4.88 | 4.75 | 3.4 | 3.4 | 2.4 | 2.5 |

The concordance of the experimental values with the calculated ones is inescapable. In disubstituted ortho compounds, some deviation is often noticed specially when the substituents have strong bond moments. This is due to the inductive and mesomeric effect of the two groups in close proximity.

In the special case when $x_1 = x_2$ ie, two substituents, are identical, we have for ortho, $\mu = \sqrt{3}m_1$ meta $\mu = m_1$, para $\mu = 0$ This is confirmed from the observations that m-dinitro benzene and-nitrobenzene have same μ-values and that p-dinitro, p-dimethyl benzenes have all $\mu = 0$

Further the observation that p-dihydroxybenzene, p-CH(OH),, has a dipole moment of 1.64 shows that the two O-H links are not in the plane of the ring but inclined to the plane, so that a net moment has resulted.

**Ionic Character of Bonding**: Consider a simple heteronuclear diatomic molecule like HCl. How the bonding electrons are located and shared between the two atoms can be somewhat assessed from calculations of dipole moment. For HCl, the dipole moment has been found to be 1.04 d and the bond-length, from infra-red spectra, to be 1.275Å. If we consider the molecule to be composed of two separate ions, hydrogen having been fully deprived of the electrons as $Cl^{-}H^{+}$, then the dipole moment would be

$\mu = (4.8 \text{ X } 10^{-10})(1.275 \text{ X } 10^{-8})$ e.s.u.= 6.1 debye.

But the measured value is only 1.04 d. If the bonding electrons were symmetrically located between the two nuclei, the dipole moment would have been zero. The ionic character is then expressed as

$$\boxed{\%\ \text{ionic} = \frac{\mu_{obs}}{\mu_{calc}} \text{x } 100 = \frac{1.04}{6.1} \text{ x } 100 = 17\%}$$

Besides these, the knowledge of dipole moments is quite helpful in the interpretation of behaviour of solutions and gases often different from their ideal states, in the explanation of solubilities and the influence of solvents on reaction rates etc.