ANISALDEHYDES: A STRUCTURAL PERSPECTIVE

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CERTIFICATE

This is to certify that the work incorporated in the dissertation

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being submitted by Mr. A. M. Vankalas for the M. Phil. degree in Chemistry was carried out by him under my supervision. Such material as has been outlined from other sources has been acknowledged in the dissertation.

Dr. J. G. Chandwadkar
(Research Guide)

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DIPOLE MOMENT IN THE GROUND STATE

I.1 Introduction :

Atoms and molecules interact with electric field essentially because of their charged constituents. Study of dipole moments of polar molecules reveals electric charge distribution within a molecule, various reactive centres, interactions with electromagnetic radiations etc. At present various techniques [1,2] are at disposal for the determination of molecular structure, each with its own limitations. Knowledge of dipole moment in various states is a simple tool for judging appropriate structure out of numerous possibilities. Study of stark effect (microwave spectra), high frequency dielectric absorption, molecular beam technique etc. are some recent advances in the methodology of measuring dipole moments, however use of static dielectric constant and molar refraction for this purpose is more popular amongst the chemists because of the simplicity of the techniques.

Dielectric Constant :

Matter placed in an electric field interacts by polarization of charges on the interfaces. This polarization is like opposition or resistance effect to the applied field and results in reducing intensity of the same. This is a specific molecular property of the material measured as its dielectric constant or specific inductive capacity.(Fig.1d).

Formally dielectric constant (D) of a material is defined as the ratio between electrical capacity of a condenser when the substance in question forms the dielectric and electrical capacitance when a vacuum lies between the electrodes.

Polarizability and dipole moment of molecules

The electrons and nuclei in any molecule are, to some extent, mobile and so when the molecule, whether it is polar or non-polar, is placed in an electric field, there will be a small displacement of the electrical centres with the result that a dipole, in addition to one which may already be present, will be induced in the molecule. If $\mu_{g,i}$ is the electrical moment of the induced dipole, produced by a field of intensity F acting on a single molecule, then

$$\mu_{g,i} = \alpha F \qquad \ldots \quad \ldots \quad (I.1)$$

The constant α is called the polarizability of the molecule. It is a measure of the ease with which the molecule can be polarised, that is the ease of displacement of positive and negative charges with respect to each other, in an electric field.

The product of the vector distance $\vec{d}$, between the centres of positive and negative charges and the resultant negative charge 'e' gives the magnitude μ_g of the dipole moment.

$$\mu_g = \vec{d}\, e \qquad \ldots \quad \ldots \quad (I.2)$$

The molecular distances are of the order of 10^{-8}cm and electronic charge is of the order of 10^{-10} e.s.u. Hence, dipole moment will have an order of 10^{-18} e.s.u. cm. Conveniently, this magnitude is called as 1 Debye. The

SI unit for dipole moment is Coulomb meter (C m), which is related to Debye unit as, 1 Debye = 3.334×10^{-30} Cm.

I.2 Molar Polarization :

The relationship between dielectric constant and polarizability was first deduced by Clausius[3] and Mosotti[4] and the expression for the molar polarization (P)

$$P = \frac{D-1}{D+2} \cdot \frac{M}{d} = \frac{4}{3} \pi N \alpha \qquad \ldots\ldots \quad (I.3)$$

is known as the Clausius-Mosotti equation, where, M and d are the molecular weight and the density of the substance respectively and N is the Avogadro's number. It is now realised that the assumption of a small spherical cavity containing a unit charge, on which the above deduction is based, is only an approximation, and hence the equation cannot be regarded as exact. It is strictly applicable to non-polar gases and probably reasonably accurate for a gas at low pressure where the static dielectric constant is close to unity.

Contributory Parts of Molar Polarization:

The molar polarization consists of (1) the distortion polarization (P_d) and (2) the orientation polarization (P_o).

(1) The distortion polarization (P_d) resulting from induction or deformation is due to the elastic displacement of the charges in the atoms and molecules under the action of electric field. This distortion polarization is the sum of the electronic (P_e) and atomic (P_a) polarization.

(2) The orientation polarization (P_o) is due to the orientation of the permanent dipoles in the direction of the applied field. In case of non-polar molecules, there is no contribution due to the orientation polarization.

<u>Electronic Polarization</u>:

Electronic polarization (P_e) exists in all atoms and molecules of both polar and non-polar dielectrics resulting from the elastic displacement of the electron charge cloud relative to the nuclei when the atom or molecule is acted upon by an electric field. Its magnitude when referred to 1 mole of the dielectric substance is, $P_e = 4\pi N\alpha_e/3$ where α_e is the electronic polarizability.

Substitution of the Maxwell relation[5], $D = n^2$, in the equation (I.3) where n is the refractive index, gives

$$P_e = \frac{4}{3}\pi N\alpha_e = \frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = R$$

the Lorentz- Lorentz expression[6,7] for the molar polarization (R) for visible light.

Laplace[8] derived the formula, $P_e = (n^2-1)\ M/d$. It was found, however, that for liquids this relationship was not sufficiently independent of temperature. Gladstone and Dale[9] proposed the expression $P_e = R = (n-1)\ M/d$. The molar refraction calculated from this equation was found to be constant for gases [10,11]. Eykman[12] found that the required independency of temperature was better secured by the relation $P_e = (n^2-1/n + 0.4)\ M/d$. Since this formula does not quite answer the purpose and moreover is purely empirical, it has not found general acceptance.

Atomic Polarization :

In an electric field, not only the electron-clouds but the actual nuclei of the atoms forming the molecule are also affected, being displaced relative to one another. This form of polarizability of the molecule is usually called the atomic polarizability α_a and the polarization corresponding to it as the atomic polarization P_a. The magnitude of the atomic polarization is given by the expression, $P_a = 4\pi N\alpha_a/3$, where α_a is the atomic polarizability. For polar molecules, atomic polarization can be determined by plotting the molar polarization of a compound against the reciprocal of absolute temperature. A best straight line is drawn through the points and the intercept on polarization axis represents the distortion polarization ($P_d = P_e + P_a$). Knowing the value of the electronic polarization P_e it is possible to calculate the atomic polarization P_a. Jenkins[13] showed that the application of this method for measurement on solutions is unsound owing to the variation of apparent moment of a solute with dielectric constant of the solvent. Atomic polarization can also be evaluated by using Fuch's[14] dispersion formula and by indirect method[15] which consists of the dielectric constant measurement of a given substance in the solid state at a temperature lower than the melting point. Since the dipoles cannot orient under these conditions, the molar polarization calculated from Eq. I.3 will be distortion polarization. The atomic polarization will then be, $P_a = P_d - P_e$. The ideal method for determination of atomic polarization of a polar compound involves the measurement of refractive index in the infrared region. Measurement of refractive index with infrared radiations is difficult and values of P_a are generally determined indirectly. For most substances, they are small, not more than 2 or 3 cc and as a rough approximation, they may be taken as 5 or 10 per cent of P_e for the D-line of sodium.

Orientation Polarization:

The term orientation polarization (P_o) arises in case of polar molecules from the fact that the electric doublets are oriented by the applied field so that the positive ends of the permanent dipoles point towards the negative charged plate, so; the intensity of the field within the medium is thus diminished as compared with that in a vacuum and hence the dielectric constant exceeds unity by an appreciable amount. Substances with permanent moment thus generally have high dielectric constants. The polarizability due to orientation of molecules is called as the orientation polarizability α_o.

Thus, the total molar polarization P of polar dielectrics in an applied field is given by

$$P = P_d + P_o$$

$$= P_e + P_a + P_o \qquad \cdots \quad \cdots \qquad (I.4)$$

and the total polarizability of the molecule α as

$$\alpha = \alpha_d + \alpha_o$$

$$= \alpha_e + \alpha_a + \alpha_o$$

I.3 Static Dielectric Constant and Dipole Moment:

Debye Equation :

Debye[16,17] studied the behaviour of polar dielectrics in an electric field considering following approximations : The field has no perturbing effect on the magnitude of the dipole moment of the molecule. The dipoles may assume any position relative to the direction of the applied field and the energy of dipole-dipole interaction is insignificant in comparison with the energy of thermal motion. He derived an expression, $\alpha_o = \mu^2_g / 3kT$, correlating the permanent dipole of the molecule μ_g and its orientation polarizability α_o. In this equation k is Boltzmann's constant and T is the absolute temperature. Thus, the overall expression for the polarizability of the molecule is

$$\alpha = \alpha_e + \alpha_a + \frac{\mu_g^2}{3kT} \quad .. \quad (I.5)$$

Substituting the above value of α in the Clausius-Mosotti formula,

$$P = \frac{D-1}{D+2} \cdot \frac{M}{d} = \frac{4}{3}\pi N(\alpha_e+\alpha_a+\frac{\mu_g^2}{3kT}) \quad .. \quad (I.6)$$

From equation I.5 and I.6, the orientation polarization comes out as $P_o = 4\pi N\mu^2_g / 9kT$.

The Debye formula (Eq. I.6) include all the limitations inherent in the Clausius-Mosotti equation and it is therefore approximate and can be applied only to polar gases at very low pressures and also in rough approximation to extremely dilute solutions of polar subtances in non polar solvent. In considering the theory of polar dielectrics, Debye also took no account of the reactive (internal) field of the molecules.

Onsager Equation:

Onsager[18] was the first to provide a satisfactory alternative to the Mosotti-Debye relation. In the Mosotti field the molecule is imagined at the centre of a larger (hypothetical) cavity within the medium. Onsager replaces this with a spherical cavity of the size of the molecule, which is assumed to be an isotropically polarizable molecule carrying its dipole moment in a very small volume located at its centre. In an electric field, the total electric moment $\mu_{g,T}$ per molecule in the direction of the field is composed of the permanent dipole moment μ_g of the molecule of a polar dielectric and the deformation moment created in the so-called (effective) field (αE_{loc}). Thus, $\mu_{g,T} = \mu_g + \alpha E_{loc}$. The essence of Onsager's theory is that the local (effective) field is separated into two components: the cavity field G and the reaction field R. Thus, $E_{loc} = G + R$. Theoretical calculations give the following expressions for G and R :

$$G = \frac{3D}{2D+1} R, \qquad R = \frac{2(D-1)}{2D+1} \cdot \frac{\mu_{g;T}}{a_o^3}$$

where a_o is the radius of the spherical cavity of the size of the molecule. Using these expressions, Onsager derived the following equation :

$$\frac{(D-n)^2 \, (2D+n^2)}{D\,(n^2+2)^2} \cdot \frac{M}{D} = \frac{4\pi N \mu_g^2}{9kT} \quad \ldots \ldots \quad (I.7)$$

Onsager's concept had universal appeal. Number of critics[19-26] have tried to assess and improve this basic equation. Even at present number of attempts are being made in the same direction[144-147].

Next major development in the theory was made by Kirwood[27]. He pointed out that hindered rotation must play an active part in the dielectric polarization of polar liquids and must be responsible for the large departure from the Lorentz field. Besides it should be introduced not to supplement but to correct the Lorentz field. He proposed the equation :

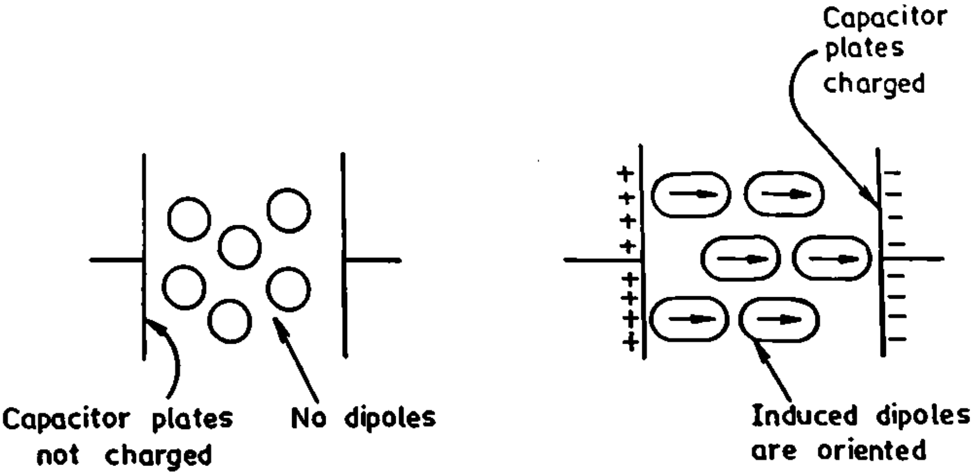
$$\frac{(D-1)\,(2D+1)}{g \cdot D} \cdot \frac{M}{d} = \frac{4\pi N}{3} \left(\alpha_d + \frac{g\,\mu^2}{3kT}\right)$$

where 'g' = $1 + Z \cos \gamma$ and Z is the number of closest neighbours of a given molecule. $\cos \gamma$ is the mean value of the Cosine of the angle between the direction of the dipoles of two neighbouring molecules. The correlation parameter'g' would be unity on the Onsager model, where the molecule is regarded as being immersed in a continuous medium of uniform dilectric constant. Experimental data, however, indicates that it may deviate appreciably from unity and that the deviation may be either positive or negative. For example g is 1.1 for nitrobenzene and 4.1 for hydrogen cyanide, but only 0.9 for pyridine. Positive deviations would be expected when short range hindering torques favour parallel orientations of the dipoles of neghbouring molecules and negative deviations when they favour antiparallel orientation.

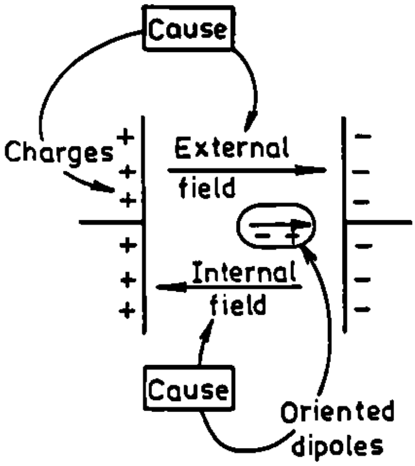
Determination of exact 'g' value is the main difficulty in the application of this equation, which is normally obtained by X-ray data.

Many workers[28-41,48-72] have attempted to modify these relations between dipole moment, dielectric constant, refractive index in solution and gas phase; modifying the basic concepts outlined in Fig.I.a-Ii

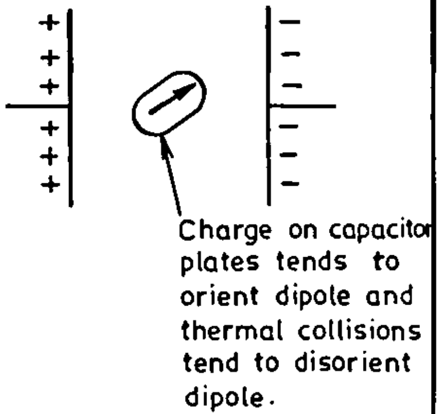
The concept proposed by Jatkar et.al[41,42] was that the molecules should not be considered as spherical shaped like in Onsager and Kirkwood theory but those should be treated as needle shaped and hence total anisotrophic. The orientation of these needle shaped molecules should be



Fig·1a: The charge on the capacitor plates induces dipoles in the molecules of a dielectric·(polar or nonpolar)·



Fig·1b: The orientation of dipoles in the dielectric sets up an internal field which is directed counter to the external field produced by the charges on the plates·



Fig·1c: The permanent dipole of the dielectric are subject to an electrical orienting force and a thermal disorienting force·

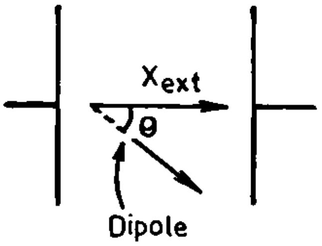
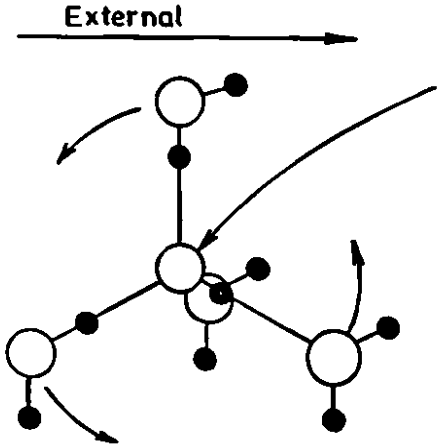


Fig.1d: An example of a dipole at an angle θ to the external field.

Fig.1e: The average moment $<\mu>$ of a gas dipole

$$<\mu> = \frac{\mu^2 X_{ext}}{3kT}$$



When this water molecule wants to align with the external field the whole cluster must align.

Fig.1f: When the central molecules of the tetrahedral group tries to align with the external field, the whole group aligns.
$g = 4$ and $\cos \gamma = 1/3$

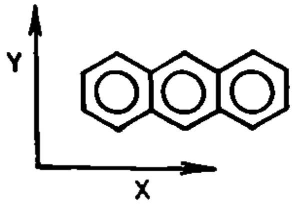


Fig.1g: Polarizability of a large molecule along different axes is not same.

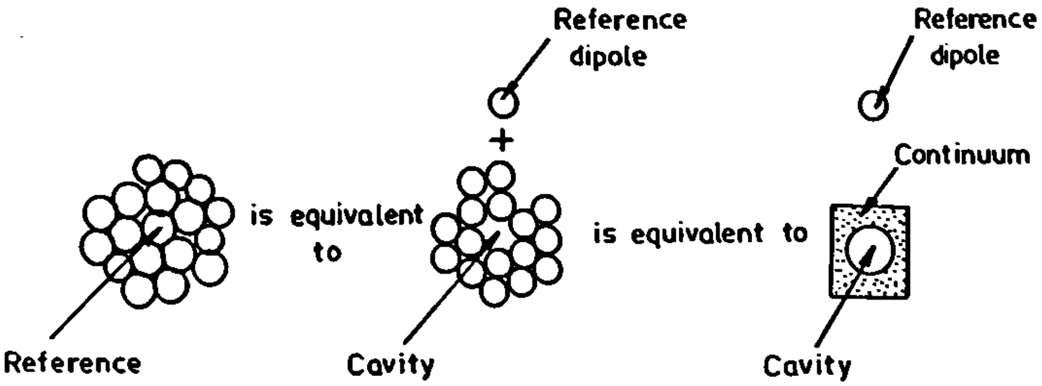


Fig. 1h:The approximately spherical cavity into whih a reference dipole or group of dipoles is caged.

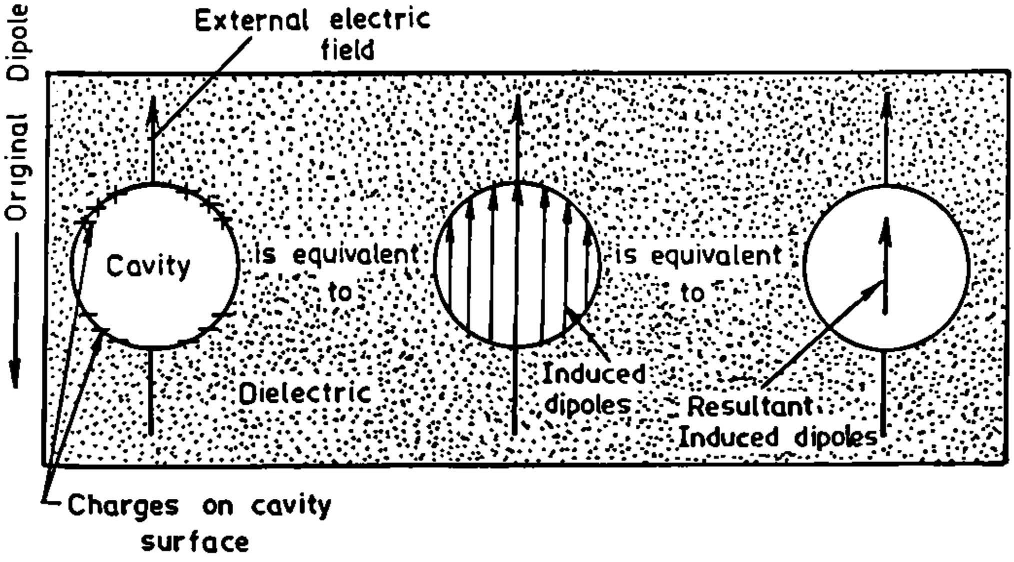


Fig 1i The electrical effect of a cavity is equivalent to the effect of a single dipole.

quantized, assuming quasicrystalline nature of liquid dielectrics. The resulting equation is

$$P = (D-1)\frac{M}{d} = 4\pi N\alpha_e + \frac{4\pi N\mu_g^2}{3kT}\left(\frac{J+1}{J}\right) \quad \ldots (I.8)$$

$J = \infty$ for gases and 1/2 for solids and liquids. There have been subsequent modifications suggested to this equation also[44,47,114].

I.4 Solvent Effect and Evaluation of Dipole Moment from Measurement of Dilute Solutions.

Muller[73-76] was the first to show that the dipole moments calculated from the experimental results for dilute solutions by means of the Debye formula differ from their dipole moment values in the gas phase. This phenomenon has acquired the name as solvent effect. The main cause of the existence of the solvent effect is that the Debye formula, which is based on the theory of the local Lorentz field, cannot take into account the electrostatic interaction arising between molecules of the solute and those of the solvent surrounding them. In all the cases studied by Muller, the apparent dipole moment in solution was less than the moment in the vapour state, but it was soon realised that this can not be generalised. There are number of instances where the apparent moment in solution is greater than that for the vapour. The former is known as a negative solvent effect and the latter a positive solvent effect. The solution moment values were calculated from polarization ($P_{2\infty}$), obtained by extrapolating polarization-concentration curve to zero concentration. There have been innumerable attempts to derive equations relating either $P_{2\infty}$ or the apparent dipole moment of a substance in solution with the dielectric constant of the medium. The approaches to the problem are discussed in the present section.

In extremely dilute solutions, the molecules of poler substances must behave just as in the vapour state and must become freely oriented in the applied field. Hence, Debye [17] considered that the method of finding the dipole moment in gaseous state can be applied to dilute solutions with satisfactory approximation. Assuming additivity of the properties of the components of the solution, the expression for molar polarization of the solution (P_{12}) can be written as

$$P_{12} = P_1f_1 + P_2f_2 = \frac{D_{12}-1}{D_{12}+1} \cdot \frac{M_1f_1 + M_2f_2}{d_{12}}$$

Where P, f and M are the polarization, mole fraction and molecular weight respectively and the suffixes 1, 2 and 12 refer to the solvent, solute and solution respectively. Since, $f_1 + f_2 = 1$, the molar polarization P_2 of the solute will be $P_2 = P_1 + (P_{12} - P_1)/f_2$. If the concentrations are expressed in weight fractions (W), the corresponding expression [77] for specific polarization P_2 of solute will be

$$P_2 = P_1 + (P_{12} - P_1)/W_2 = \frac{D_{12} - 1}{D_{12} + 2} \cdot \frac{1}{d} \qquad \ldots(I.9)$$

and

$$P_2 = P_2 M_2$$

The value of P_2 so computed are then plotted against f_2 or W_2 and the resulting curve is extrapolated to f_2 or $W_2 = 0$. The intercept, so obtained, is taken as the value of P_2 at zero concentration (or infinite dilution), $P_{2\infty}$. Then the dipole moment can be calculated using an expression

$$P_o = P_{2\infty} - (P_e + P_a) = 4\pi N\mu_g^2 / 9KT \qquad \ldots(I.10)$$

or

$$\mu_g = 0.01283 \sqrt{(P_{2\infty} - P_e - P_a)T} \cdot 10^{-18} \text{ e.s.u.}$$

Jatkar equation can be applied to find out the molar and specific polarizations of solution as follows :

$$P_{12} = (D_{12} - 1)\ (M_1f_1 + M_2f_2) / d12 \qquad \ldots(I.11)$$

$$P_{12} = (D_{12} - 1)/ d_{12} \qquad \ldots(I.12)$$

Since $P_1 = (D_1 - 1)/d_1$, it follows, from Equations I.9 I.10 and I.11 that

$$P_2 = \frac{D_1-1}{d_1} \cdot M_2 + \left[\frac{D_{12}-1}{d_{12}} - \frac{D_1-1}{d_1}\right] \frac{M_2}{W_2}$$

and

$$P_o = P_2 - (p_e + P_a) = \frac{4\pi N\mu_g^2}{3\ kT} \cdot \frac{j+1}{j}$$

In solution (2j + 1) increases from 2 to 3, 4, 5 and infinity only at zero concentration[78].

Hedestrand [79] pointed out that if the dielectric constant and density of the solutions vary linearly with the mole fraction of the solute, they can be expressed as $D_{12} = D_1(1 + \alpha f_2)$ and $d_{12} = d_1(1 + \beta f_2)$ respectively, where α and β are the slopes of the straight lines describing the dependence of D_{12} and d_{12} on f_2. From the relations, he derived the following equation for $P_{2\infty}$.

$$P_{2\infty} = \frac{3\alpha D_1}{(D_1+2)^2} \cdot \frac{M_1}{d_1} + \frac{D_1-1}{D_2+2} \cdot \frac{M_2-M_1\beta}{d_1}$$

Hedestrand realized that, in certain circumstances the assumption that D_{12} is linear with f_2 over the concentration range studied is not justified and in such cases suggested that α should be taken as limiting value of $\Delta D_{12}/f_2 D_1$, as zero concentration is approached.

Many workers[80-90] have suggested modifications in these methods.

The equation suggested by Halverstadt and Kumler[91] has been widely used. They assumed linear dependance of the dielectric constant and the specific volume (v) of the solution on the weight fraction of solute i.e. $D_{12} = D_1 + \alpha W_2$ and $v_{12} = v_1 + \beta W_2$. From these relations they have derived an equation for the molar polarization at infinite dilution as

$$P_{2\infty} = \left[\frac{3\alpha v_1}{(D_1 + 2)^2} \quad \frac{D_1 - 1}{D_1 + 2} \ (v_1 + \beta) \right] M_2 \quad \ldots (I.13)$$

The molar refraction of the solute may also be derived from the measured values of the refractive index by utilizing the relationship.

$$R_2 = \left[\frac{3\gamma v_1}{(n_1^2 + 2)^2} + \frac{n^2{}_1 - 1}{n_1^2 + 2} (v_1 + \beta) \right] M_2$$

which is analogous to Equation I.13 but with D replaced by n^2 and α by γ, the value of dn_{12}^2 / dW_2.

Equation I.13 has been widely adopted, since the use of the concentration expressed in weight fractions of the solute considerably simplifies the calculations. In this connection, Hedestrand[79] expresses the concentration in mole fraction in the calculations of α and β. The definition of $\beta = dv_{12}/dw_2$[91] instead of d_{12}/df_2[79] has also been considered by Halverstadt and Kumler.

Higasi[92] proposed an equation in which all parameters except the dielectric constant were completely absent:

$$\mu_g = B\ (\Delta D_{12}/f_2)^{1/2} \qquad \text{.. (I.14)}$$

where 'B' is a constant depending on the nature of the solvent and temperature. For benzene at 25°C, 'B' = 0.90 ± 0.1 and for hexane it is 1.15 ± 0.1 . Somewhat later, Bal and Srivastava[93] gave a more accurate value of 'B' for benzene as 0.828. They have also shown that Higasi equation is valid for straight part of the D_{12}-f_2 curve. Higasi[94] proposed a modification in Eq. I.14 and suggested another form as $\mu_g = B\ (a_o - a_D)^{1/2}$, where a_o and a_D are the slopes of D_{12}-f_2 and n^2_{12}-f_2 curves respectively. Vij and Shrivastava[95] have shown that if the term a_D be changed to a_∞ , where a_∞ is the slope of $n^2_\infty - f_2$ curve, the equation would provide better results. The term n_∞ represents the refractive index of solutions measured at a frequency where the permanent dipoles are unable to follow the alternations. Shrivastava and Charandas[96] have proposed an analogous equation in which the concentration of solute is expressed in weight fraction.

$$\mu_g = A\ (M_2\alpha)^{1/2}$$

where 'α' = d $(D_{12})/dW_2$ and 'A' = $0.012812\,[3T/d_1(D_1+2)^2]^{1/2}$. Jai Prakash[97] has shown that Higasi's equation is a special case of general Debye equation and applies to those cases where static dielectric constant of the solution is equal to or close to unity and modified Higasi equation as

$$\mu_g = A'(M_2\,\alpha T)^{1/2} \quad \text{where } 'A'' = A/T^{1/2}.$$

Guggenheim[98] suggested a method, based on the Debye equation, of calculating the moment by plotting a quantity $\Delta = (D_{12} - n_{12}^2) - (D_1 - n_1^2)$ against the concentration C (moles per ml) of polar solute in solution state. The intercept $(\Delta/C)_0$ of the curve at C = 0 is then used to calculate the moment by means of the equation.

$$\mu_g^2 = \frac{9kT}{4\pi N} \cdot \frac{3}{(D_1+2)\,(n^2+2)} \cdot \left(\frac{\Delta}{C}\right)_0$$

He has recalculated the data on a few dichloronaphthalenes in benzene solution, finding that his method gives good agreement with those obtained from polarization-extrapolation method. In this method, the determination of the density of the solution is necessary only to calculate the concentration. Bottcher[99] has calculated the dipole moment of phenol from benzene solutions by Debye, Hedestrand and Guggenheim equations and obtained the dipole moment values as 1.59, 1.60

and 1.59 D respectively. Block and Iwacha[100], Few and Smith[101] and Iyengar[102] have shown that the Guggenheim equation does not give reasonable results.

Similar attempts have been made by Palit[103], Smith[105], Scholte[106], Fujita[107], Meyyappan and Arunachalam[108], Grunwald[110], Finsy[111], Guha[112], Petrosyan[113], etc.

Modified Jatkar Equation :

Deogadkar[114] and Patil[115] suggested some modifications in the Jatkar equation [41,42]. According to them in highly dilute solution of polar molecules in nonpolar solvent, the quasicrystalline nature of liquid shall not exist. This eliminate many uncomfortable features of the Jatkar equation. The technique of Halverstadt and Kumler to use relative changes in concerned properties to estimate $P_{2\infty}$ was used by them replacing an empirical constant in place of $(j+1)/j$ in the Jatkar equation.

They derived the following equations for the molar polarization at infinite dilution ($P_{2\infty}$) and the electronic polarization (P_e).

For the concentration in weight fraction:

$$P_{2\infty} = \left[\alpha v_1 + (D_1-1)(v_1+\beta) \right] M_2$$

and

$$P_e = \left[\gamma v_1 + (n_1^2 - 1) \ (v_1 + \beta) \right] \ M_2$$

For the concentration in mole fraction :

$$P_{2\infty} = M_1 v_1 \alpha + (D_1 - 1)(M_2 v_1 + M_1 \beta)$$

The orientation polarization and dipole moment can be evaluated using the following empirical formula:

$$P_o = P_{2\infty} - (P_e + P_a) = \frac{4\pi N\mu^2 g}{3kT} \ (0.8955 \ D_1)$$

They tested the validity of modified Jatkar equations by recalculating the dipole moment values of several organic compounds in various solvents and comparing them with the ones obtained from Halverstadt-Kumler equation. They have shown that the values obtained by using modified Jatkar equation are in excellent agreement with those obtained by using Halverstadt-Kumler equation.

The object of all the extrapolation equations is to find out the total polarization at infinite dilution $P_{2\infty}$ The orientation polarization and dipole moment is then calculated by means of Eq. I.10.

The methods for the extrapolation of molar polarization of dilute solutions of polar molecules in non-polar solvents to obtain $P_{2\infty}$ have been critically examined by Taylor[116]. It has been claimed that these methods are in error when molar polarization of solvent varies with concentration. He has also shown that the preceding methods of extrapolation yield the partial molar polarization of the solute at infinite dilution, a quantity which has an unambiguous theoretical interpretation.

In conclusion, it may be noted that the methods for computing dipole moments based on the extrapolation of dielectric constant, density and square of refractive index to zero concentration of solute give small deviations of the values obtained than methods in which polarization is subjected to extrapolation.

The validity of extrapolation method is now well established. Most of the recent workers[140,141,143] in an attempt to eliminate the mutual effect of various interactions prefered to use extrapolation methods.

SECTION B

DIPOLE MOMENTS IN THE ELECTRONICALLY EXCITED STATE

I.5 Introduction:

The method of measuring dipole moment, even though anticipates an interaction with an electromagnetic field, the interaction is not so severe as to change the basic electron distribution of the molecule. However while interacting with the high energy radiation like in uv region of the electromagnetic spectrum, the interacting molecule undergoes some basic change in its electronic structure. There is hardly any method to measure the dipole moment of this rearranged structure as directly as the measurement in the ground state of the molecule.

The vapour phase absorption spectrum of a molecule certainly offers the knowledge of energy of various electronic levels within the molecule, but that is not enough to predict the electron distribution of the state.

The process of dissolution is basically electronic interactions between solute and solvent molecules. These interactions are catagorized as (i) dispersion (ii) dipoleinduced dipole (iii) dipole-dipole and multipole (iv) specific association (e.g. Hydrogen bonding) etc. Even in the electronically excited state, the same interactions exist but to different extent because the basic unit of interaction, the dipole moment is now different due to different electron distribution. Assuming that the interacting power of various solvents can be expressed in terms of their dipole moments, polarizability etc. one can estimate the differential energy of these interactions with a common solute. These are basically function of the dipole moment of the solute. With this philosophy it is obvious that electronic (UV) spectrum of a molecule in various solvents is a basic tool to estimate the dipole moment of the molecule in the excited state.

Several theoretical models have been proposed to interprete solvent induced changes in various spectral parameters such as electronic and vibrational frequencies and intensities, n.m.r., chemical shifts and spin-spin coupling constants[43,45] of solute molecules due to non-specific interactions. Most of the studies make use of the continum model (i.e. Onsager's reaction field)[18,99] to obtain an expression for changes in the spectra of polar and non-polar solvents in terms of measurable solvent parameters. Use of spectroscopic methods to study specific interactions between solute and solvent molecules is well documented in the literature.[46,104,109,129,149-153].

I.6 Classification of Absorption Bands in Aromatic Hydrocarbons:

Aromatic hydrocarbons show three main types of absorption bands which are designated by Clar[117] (as α, P and β bands) according to their intensities. The molar absorptivities of the α, P and β bands are of the order of 10^2, 10^4 and 10^5 cm^2 mol^{-1} respectively and the wavelengths where these bands are observed are generally in the order $\lambda\alpha > \lambda P > \lambda\beta$.

Benzene exhibits two intense absorption bands at about 180 nm ($\epsilon_{max} \sim 47000$) and 200 nm ($\epsilon_{max} \sim 7000$) and a weak absorption band around 260 nm ($\epsilon_{max} \sim 220$)[118]. All the three bands are associated with the electron system of benzene. The two intense bands may be ascribed to transitions to dipolar excited states, while the weak 260 nm band is ascribed as the forbidden transition to a homopolar excited state.

Different nomenclatures have been used to describe the three bands of benzene. Some of these important, systematic and accepted assignments are as follows:

Table - I.1 : Nomenclature of benzene bands[117,119-121]

Band Position/ nm	Assignement			
180	β	$^1B \leftarrow {}^1A$	$^1E_{1u} \leftarrow {}^1A_{1g}$	Second primary band.
200	P	$^1L_a \leftarrow {}^1A$	$^1B_{1u} \leftarrow {}^1A_{1g}$	First primary band.
260	α	$^1L_b \leftarrow {}^1A$	$^1B_{2u} \leftarrow {}^1A_{1g}$	Secondary band

Though the three bands of benzene are affected markedly by substitution, the general spectroscopic behaviour of substituted benzene is largely uniform and greatly resembles with that of the parent compound. Thus in benzene substituted by auxochromes, one usually finds the 260 nm band of the parent compound with its characteristic vibrational structure and the two shorter wavelength bands (corresponding to the bands observed in benzene of 200 and 180 nm) in benzene. Out of these three bands, the 200 and 260 nm bands in substituted benzene are of greater interest since both of them occur in the wavelength range normally accessible with the most of the spectro-photometers. Both the bands are of course shifted to longer wavelengths by the substitution. The spectrum of benzene is said to be perturbed by the introduction of substituents.

I. 7 Solvent Effect on Electronic Absorption Spectra and Dipole Moment in Excited State:

This effect is observed as changes in positions of the band maxima, band intensities, shapes and structures of the bands. Since band maxima are direct repurcation of the energy of the transition, most of the attempts of interpretation are focussed on this parameter. The shifts being very small at times, and the mutual cancellation or addition of many effects, are main obstacles in the observation.

In the process of solution the solute molecule, caged by solvent molecules, stabilizes because of the lowered energy of the system. The process of electronic transition by absorption of photon requires $\sim 10^{-15}$ sec. During this time, the positions of the nuclei remain unchanged because time required for a bond vibration is $\sim 10^{-13}$ sec. and for rotation it is about 10^{-10} sec. The instantaneous state of solute molecule at the time of electronic transition is therefore a non-equilibrium state called Franck-Condon state.

If the life time of the excited state is sufficiently long (10^{-8} sec.) an equilibrium is attained with the surrounding. Untill this equilibrium is attained, the solute molecule experiences 'packing strain' depending on the geometrical arrangement of the surrounding solvent molecules. The solvation energy in ground state S" changes to S', the solution energy in the Franck-Condon excited state.

Bayliss and McRae[125] have represented the effect of solvent on the electronic absorption spectra of polar and non-polar molecules in solutions in various categories as follows :

(a) Non-polar solute in non-polar solvent:

They assumed that the solution energy in the both ground and excited state, which is mainly dispersion energy in this case, remains constant. There is no solute solvent orientation or packing strain. The solution spectra normally retains the characteristics of the vapour phase spectrum.

On excitation, the non-polar molecule may become polar. The solvation energy of the excited state S' is then greater than the solvation energy in the ground state S". Consequently the energy required to excite the molecule from solvated ground state to the solvated excited state is less than that required to excite the unsolvated

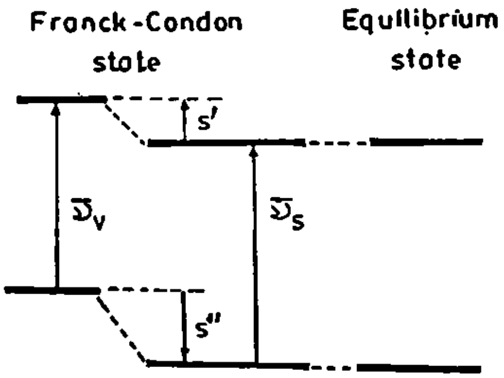


Fig. I.1

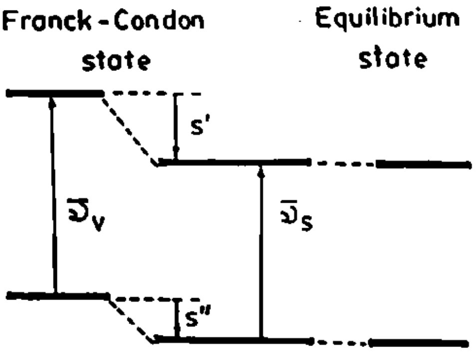


Fig. I.2

The effect of solvation energies on the solution absorption frequency when dipole-polarization forces are dominant and when there is no orientation strain, i.e. when the Franck-Condon and the equilibrium excited state have the same solvation energy : (Fig. I.1) solute dipole moment decreases, and (Fig. I.2) it increases, during the transition.

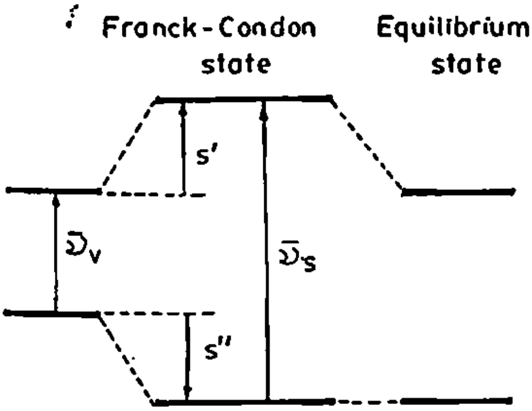


Fig. I.3

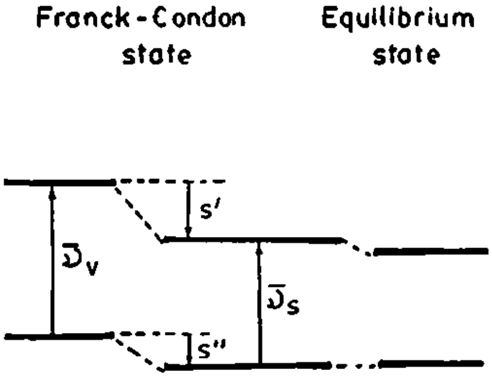


Fig. I.4

Solution spectrum when dipole-dipole forces are dominant between solute and solvent, and when there is orientation strain in the Franck-Condon excited state : (Fig. I.3) dipole moment of solute decreases, and (Fig. I.4) it increases, during the transition.

molecule. Thus occurrance of excitation at lower energy than the gas phase is called "red shift". Fig. I.1. The magnitude of this shift depends on the solvent refractive index[124].

(b) Non-polar solute in polar solvents :

As in the previous case, there is no dipole orientation and hence no packing or orientation strain existing in this case. Upon excitation if a dipole is induced, it results into red shift as described earlier. However since solvent cage structure is stronger due to the polarity, the packing strain may be little higher.

(c) A polar solute in non-polar solvent :

Even in this case the orientation strain is minimum because of the non-polar nature of the solvent. The main contributors to the solvation energy are dispersion forces and dipole induced dipole forces.

Upon excitation the dipole moment μ_e may increase or decrease than ground state dipole moment μ_g, depending upon electron distribution in the excited state. Two cases arise-

(i) if $\mu_e > \mu_g$ the solvation energy $S' > S''$ and red shift is observed as explained earlier. The shift depends upon the refractive index of the solvent (Fig. I.2)

(ii) if $\mu_e < \mu_g$ the solvation energy S' $<$ S" and one obviously expects a blue shift. This blue shift is superimposed on the polarization red shift and the resultant shift, which may be red or blue is observed (Fig. I.1)

(d) Polar solute in polar solvent :

Even in this case the dipole moment in the excited state μ_e may be greater than or smaller than the ground state dipole moment depending upon the electron distribution in the excited state. The solute-solvent dipolar interactions are strong in the ground state, with a good orientation strain.

(i) if $\mu_e < \mu_g$; the S' $<$ S" and the orientation strain decreases. If μ_e becomes zero; the solute becomes non-polar in a polar solvent cage. This contributes a negative term to the Franck-Condon solvation energy and it is equal to the energy required to orient the polar solvent molecules around a non-polar solute. This gives rise to a blue shift. The magnitude of this shift depends upon the difference between μ_e and μ_g (Fig. I.3)

(ii) if $\mu_e > \mu_g$; & S' $>$ S" i.e. if the solute dipole moment increases upon excitation the resultant is necessarily a red shift (Fig. I.4)

I.8 Theoretical Expressions for the Solvent Shifts:

As mentioned in the first section, the polarizability 'α' of a molecule is related to its refractive index 'n' and hence most of the expressions contain terms $(n^2-1)/(n^2+2)$ or $(n^2-1)/(2n^2+1)$.

The dispersion term is normally small and given by London [123] as

$$U_{(r)} = -\frac{3}{2}\frac{h}{r^6}\left[\frac{\nu_1 \cdot \nu_2}{\nu_1 + \nu_2}\right]\alpha_1 . \alpha_2$$

Here the α' s are the polarizabilities and νs arise from the ionisation energies, $h\nu_1$ and $h\nu_2$ for the molecules, h being Planck's constant. These forces are always attractive, whatever the mutual orientation of the molecules. They are additive vectorally (by the parallelogram law) between groups of molecules and, they are independent of temperature.

For the total interaction energy between two similar polarizable dipole molecules in the gas phase, one can write the expression[123] as under

$$U_{(r)} = \frac{b}{r^n} - \left[\frac{2}{3} \cdot \frac{\mu^4}{kT}\ \frac{1}{r^6}\right] - \left[\frac{2\mu^2\alpha}{r^6}\right] - \frac{3}{4}\left[\frac{h\nu\alpha^2}{r^6}\right]$$

= Repulsion - Dipole--dipole + Dipole induced dipole + Dispersion

$$= \frac{b}{r^n} - \frac{1}{r^6}\quad \underset{\text{I}}{\frac{2\mu^4}{3kT}} + \underset{\text{II}}{2\mu^2\alpha} + \underset{\text{III}}{\frac{3}{4}\ h\ \alpha^2}$$

$$U_{(r)} = \frac{b}{r^n} - \frac{C1}{r^6}$$

Bayliss[124] derived following equation for the frequency shift $\Delta\bar{\nu}$ caused by the solvent.

$$\Delta\bar{\nu} = \text{Constant} \times \left[\frac{f}{\bar{\nu}_v \, a_o^3} \right] \frac{n^2-1}{2n^2+1}$$

where 'f' is the oscillator strength, 'a_o' radius of the spherical molecule, 'n' the refractive index of the solvent and $\bar{\nu}_v$ is the frequency of absorption maximum in the gas phase.

It is appropriate to mention here that most of these theoretical developments are based on Onsager's Reaction Field[18] which in brief can be described as : (Fig. 1h)

The solute molecule is to be considered as a point dipole at the centre of a spherical cavity of radius a_o immersed in a homogeneous solvent dielectric. The electrostatic interactions between the solute dipole μ and dipole induced in the solvent dielectric due to the former give rise to the induction and orientation polarization. As a result of these polarizations an effective electric field 'R' is set up in direction opposite to that of the point dipole (induced moment is always oriented in the opposite direction of the orienting field). Due to this reaction field,the dipole moment in solution μ' is changed from the dipole moment in gas phase value μ by an amount $\alpha R'$, where α is the electronic polarizability of the molecule. Thus

$$\mu' = \mu + \alpha R$$

'α' is considered as a scaler quantity and in most organic molecules $\alpha = a_o^3/2$. Based on these considerations the reaction field 'R' is given by the expression.

$$R = (2\mu/a_o^3) \frac{(D-1)}{(D+2)}$$

R can be thought of to be composed of two parts

$$R = R_{ind} + R_{or}$$

where $R_{ind} = (2\mu/a_o^3)\ (n^2-1)\ /\ (n^2+2)$ and

$$R_{or} = (2\mu/a_o^3) \left[\frac{(D-1)}{(D+2)} + \frac{(n^2-1)}{(n^2+2)} \right]$$

The most uncomfortable part of this expression is a_o which is not well defined and hence all subsequent theories, based on Onsagar reaction field, suffer from inaccuracy of the excited state dipole moment. The only alternative is to compare frequency shifts in fluorescence spectra and the electronic spectra, the ratio being related to dipole moment without reference to a_o[137,138,148].

Many other authors have developed quantitative theories of this type. We outline here relevant McRae and Suppan theories. McRae[125,127] derived an expression for the solvent induced frequency shift, from the second order perturbation theory, taking into account all the types of interactions suggested by Bayliss and McRae[125]. On the basis of a simple electrostatic model, the frequency shift, $\Delta\bar{\nu}$, is related to the refractive index and the static dielectric constant of the solvent by an equation consisting of four terms which can be simplified by substituting the refractive index for the sodium-D-line (n) in place of refractive index at zero frequency (n_o). The simplfied form of the McRae expression may be written as

$$\Delta\bar{\nu} = \left[(A + A') + B\right] \frac{n^2-1}{2n^2+1} + C\left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right] + E\left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right]^2 \qquad \ldots \; \ldots \qquad (I.15)$$

Here the constants (A+A') represent the contribution of dispersion effect and the other constants

$$B = (\mu_g^2 - \mu_e^2)/hca_o^3 \qquad \ldots \; \ldots \qquad (I.16)$$

$$C = 2\mu_g(\mu_g - \mu_e)/hca_o^3 \qquad \ldots \; \ldots \qquad (I.17)$$

and

$$E = 6\mu_g^2(\alpha_g - \alpha_e)/hca_o^6 \qquad \ldots \; \ldots \qquad (I.18)$$

are functions of the ground and excited state dipole moments (μ_g and μ_e) and the corresponding polarizabilities (α_g and α_e) of the solute molecule with h, c and a_o being the Planck's constant, speed of light and the cavity radius respectively.

In Eq. I.15 the first term $(A+A')\ (n^2-1/2n^2+1)$, the dispersion term, represents the contribution of dispersion forces between the solute and solvent molecules, which usually gives a red-shift of absorption. The dispersion term depends in a complicated way on various spectroscopic properties of the solute and solvent molecules. The second term $B(n^2-1/2n^2+1)$ is the contribution due to interactions between permanent dipoles of solute and solvent dipoles thereby induced. The third term $C\left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right]$ corresponds to the contribution from interactions between permanent dipoles of the solute and solvent molecules. The last term $E\left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right]^2$ represents the contribution from interactions between permanent dipoles of solvent molecules and solute dipoles thereby induced, which may be regarded as the quadratic stark effect. It is assumed that the contribution of the quadratic Start effect is small compared with other contributions, hence the last term was dropped[128,129]. Thus,

$$\Delta\bar{\nu} = \left[(A+A') + B\right]\frac{n^2-1}{2n^2+1} + C\left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right] \quad .. (I.19)$$

For non-polar solvents ($D \simeq n^2$), the Eq. I.19 reduces to

$$\Delta\bar{\nu} = \left[(A+A') + B\right]\frac{n^2-1}{2n^2+1} \quad .. (I.20)$$

Various other theories and attempts to generalise the effect of solvents on spectra have been made by several workers[130-134].

According to Suppan[135], a comprehensive theory may not always be necessary in order to have a quantitative understanding for the interactions of a solute-solvent molecules. These interactions can be listed as (i) dispersion forces, (ii) dipole induced dipole interactions, (iii) dipole-dipole interactions, (iv) (higher) multipole interactions, (v) specific associations (hydrogen bonding, etc.) and (vi) solvent cage strains. Fortunately, in most cases, it is possible to neglect all but one or two of these interactions and the theories derived for such restricted cases can be quite simple and straight forward in their application. The treatment by Suppan is based on the classical Onsager model of dielectric which shows, how data like dipole moments and polarizabilities of excited states can be obtained from solvent shift experiments. Restricting for the moment to the case of a non-polarizable dipole, Suppan has given the following equation, Eq. I.21, for relative solvent shift of an electronic absorption band due to dipole-dipole interaction only, in solvent 1 with respect to solvent 2 for the given solute.

$$-\Delta E_{1\rightarrow 2} = (\mu_e - \mu_g)\mu_g \frac{\Delta f(D)_{1\rightarrow 2}}{a_o^3}$$

where $\Delta E_{1\rightarrow 2}$ is the observed energy shift of a solute absorption band between solvent 1 and 2, a_o is the radius of the (spherical) cavity occupied by the solute molecule in any of the solvent as it is assumed that $a_{o1} = a_{o2}$; $(\mu_e - \mu_g)$ is the change in the dipole moments of the solute between the excited and ground state, f (D) is the function equal to 2(D-1)/(2D+1) of a series of solvents with comparable values of refractive indices, but different static dielectric constants and $\Delta f(D)_{1\rightarrow 2}$ is the corresponding change in the function f(D) between solvent 1 and 2. It is assumed that in a particular solvent the radius of the cavity occupied by the solute molecule in the ground state (a_o) is the same as that in the excited state (a_e) i.e. $a_o = a_e$ and the molecular volume does not change appreciably on excitation. The condition $a_o = a_e$ assumes also that dipoles μ_g and μ_e are centred at the same point in the molecule.

The effect of the polarizability of the solute molecule is introduced by Suppan as a separate term independent of the dipole-dipole interaction term and it was called as the dipole-induced dipole interaction term. The polarizability change in the direction of a permanent dipole moment μ_g is $\Delta\alpha_{g-e}$ given by Eq. I.22, again for solvents with comparable value of refractive index.

$$-\Delta E_{1\rightarrow 2} = \Delta\alpha_{g-e}\frac{\mu_g^2}{a_o^6}\Delta f^2(D)_{1\rightarrow 2}$$

where $\Delta\alpha_{g-e}$ is the change in polarizability of the solute molecule in the ground and excited states.

Suppan raised some objections to the theories[126,133] wherein the dispersion interactions lead to a 'general redshift' which depends, among other things, on the oscillator strength (i.e. the intensity) of the absorption bands. He has put forth an alternative theory of the solvent shift due to dispersion forces by considering London dispersion theory and derived an expression.

$$\Delta E_{1\rightarrow 2} = -C'\frac{\Delta\alpha_{g-e}}{a_o^3}\Delta\phi(n^2)_{1\rightarrow 2} \quad \ldots\ldots(I.23)$$

where $\phi(n^2)$ is the function equal to $\frac{n^2-1}{n^2+2}$ and $\Delta\phi(n^2)_{1\rightarrow 2}$ is the corresponding change in the functions $\phi(n^2)$ between solvent 1 and 2 and $C' = 1.8 \times 10^{-11}$ c.g.s. units. Thus, he has shown that the solvent shift can be attributed to a change in polarizability on excitation and the oscillator strength plays no part.

The theory of solvatochromic shifts in solvents of different dielectric constants and refractive indices is used[136-139] to measure both the absolute value and the direction of dipole moment vectors in excited states. An expression for the solvatochromic shift for polar molecules (excluding effect of specific associations and some special solvent anomalies) is given as[139]

$$- \Delta E_{1 \rightarrow 2} = \frac{\mu_g (\mu_e - \mu_g)}{a_o^3} \left\{ \Delta \left[f(D) - f(n^2) \right]_{1 \rightarrow 2} \right\} + \frac{\mu_e^2 - \mu_g^2}{a_o^3} \Delta f(n^2)_{1 \rightarrow 2} \quad (I \cdot 24)$$

where the first term is the permanent dipole interaction term, the second term represents the stabilization difference of the ground state dipole μ_g and the excited state dipole μ_e by the induced dipoles in the solvent and $f(n^2)$ is the function equal to $2(n^2-1)/(2n^2+1)$ and $\Delta f(n^2)_{1 \rightarrow 2}$ is the corresponding change in the functions $f(n^2)$ between solvent 1 and 2. For non-polar solvent ($D \simeq n^2$) Eq. I.24 reduces to

$$- \Delta E_{1 \rightarrow 2} = \frac{\mu_e^2 - \mu_g^2}{a_o^3} \Delta f(n^2)_{1 \rightarrow 2} \quad (I \cdot 25)$$

The $f(n^2)$ plot of the solvatochromic shifts for polar solute molecules in a series of non-polar solvents can provide a measurement of the absolute excited state dipole moments. When used in conjunction with the f (D) plot in a series of polar solvents of the same refractive index, information is also obtained about the direction of the excited state dipole vector with respect to the resultant ground state dipole vector.

I.9 Limitations of the Method of Estimating Dipole Moment in Excited States[140]:

The various equations so far discussed are based on the classical dielectric model. Though of practical utility, the acutal manner of employing this approach appears to have a number of drawbacks as follows :

(1) Measurement in all sorts of solvents ranging from quite inert (e.g. cyclohexane) to quite reactive one (e.g. dimethyl sulfoxide), have been incorporated in one and the same graph.

This would imply that all solvents irrespective of their nature, structure, polarity etc., interact with the solute in an identical manner, the extent of interaction depending only on the dielectric constant of the solvent. Actually, the experimental data shows a large variation(such a variation is observed when solvents like benzene, dioxane, triethylamine, valeric acid, 1-chlorobutane, isopropyl bromide, dichloromethane etc. are used) which is obvious since the solvent interaction must also depend on its chemical nature. The extent of stabilization of the ground and excited states of the solute molecule must be different in different types of solvents. Under these circumstances, the slope of the graph of $\Delta\bar{\nu}$ vs $\Delta f(D)$ is not much meaningful.

(2) The frequency shift ($\Delta\bar{\nu}$) of the solute band is measured with respect to the band frequency in some non-polar solvent used as reference and then classifying the shift as red or blue with respect to the former. However, the choice of the reference solvent is rather subjective and the $\Delta\bar{\nu}$ so obtained is of limited significance.

(3) They cavity radius a_o in many cases is chosen in somewhat arbitrary shape for the solute molecule. In a few cases, a_o is calculated from density of the solute. The cavity radius so obtained is likely to be inaccurate; since the molecular volume in dilute solutions ($C = 1 \times 10^{-4}$ to 1×10^{-5} M) where solute molecules are essentially free from one another would be considerably different than that of pure solute in solid and liquid state. The use of equivalent shell method [138,139] is also not very satisfactory since the

solvent shell function $r = r \ (\bar{\theta}, \varphi)$ is generally not available and further the solvent shell cannot be considered is a physical continuum on the molecular level though it appears to be a statistical continuum.

Because of these drawbacks, it is difficult to access the reliability of the reported μ_e values and their implications on the related properties. The improvements against these drawbacks have been mentioned in Chapter-II of the present work.

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* * *

CHAPTER - II

CHAPTER II

EXPERIMENTAL PROCEDURE AND TREATMENT OF THE RESULTS.

The present work deals with the determination of dielectric constant, density and refractive index of organic compounds in benzene solvent. The measurements have been carried out for solutions of various concentrations at 30°C, with a view to study the effect of solvent on the dipole moment of the organic compounds. Dipole moments in the ground state (μ_g) of the various methoxybenzaldehyde isomers have been determined in benzene at 30°C.

The values of dipole moment in ground state thus obtained and solvent induced shifts of electronic absorption bands of molecules in n-pentane , n-hexane, iso-octane and cyclohexane were utilised for the estimation of dipole moments in the excited states (μ_e).

Following isomers are studied :

i) 2-Methoxybenzaldehyde,

ii) 3-Methoxybenzaldehyde,

iii) 4-Methoxybenzaldehyde.

II.A Purification of Solvents and Compounds and Preparation of Solutions:

Purification of Solvents:

Benzene : Various methods[1] are reported for the purification of benzene. The method used in the present work is the modification of the methods of Leonard and Sutton[2] and Washburn and Read[3]. Crystallisable GR grade benzene (S. Merck) was used. The traces of thiophene were removed by repeatedly shaking benzene with concentrated sulphuric acid until 'isatin test'[4] for thiophene was negative. It was then successively washed with water, dilute sodium hydroxide and water. This benzene was freed from water by keeping it over anhydrous calcium chloride. It was then subjected to repeated crystallisation by freezing. The portion which froze at 5.5°C was distilled over phosphorous pentoxide and stored over sodium in well-closed, amber glass container until required for use. This benzene was redistilled over phosphorous pentoxide just prior to use.

All the other solvents namely n-pentane, n-hexane, iso-octane, cyclohexane, diethyl ether and acetonitrile were of 'spectroscopic' grade purity, 'Fluka' (Switzerland) make, and were used without any further purification.

It was confirmed, however, that no interfering absorption in UV region was shown by all of these solvents. Special precautions were taken so as to prevent the absorption of moisture and sunlight by the solvents.

Purification of Compounds:

The various isomeric methoxybenzaldehydes (MBH)were repeatedly recrystallized from the solvents as mentioned below:

Compound		Solvent
2-MBH	. .	Pet.ether
3-MBH	. .	chloroform
4-MBH	. .	ethylalcohol

and were dried perfectly under vacuum over phosphorous pentoxide.

Purification of Benzaldehyde[4]:

Benzaldehyde is readily oxidised by atmospheric oxygen ultimately giving benzoic acid. Benzaldehyde G.R. grade (S.merck) was washed repeatedly with 10% sodium carbonate solution until no carbon dioxide gas was evolved; then with water and dried over anhydrous calcium chloride in presence of little hydroquinone or catechol (antioxidant). This benzaldehyde was double distilled under reduced pressure in the stream of nitrogen gas and stored under nitrogen gas in a well stoppered amber coloured bottle. A little quantity of hydroquinone was added to avoid its autooxidation. This benzaldehyde was redistilled in stream of nitrogen gas just prior to use.

All the purified compounds were preserved in airtight containers over phosphorous pentoxide under vacuum in a dessicator and also protected from sunlight.

Reagents :

Fused calcium chloride LR grade (BDH, England), potassium hydroxide (E. Merck) and sodium hydroxide, phosphorous pentoxide, concentrated sulphuric acid, pet. ether, chloroform, and ethyl alcohol of Sarabhai Merck AR/GR grade were used for purification of solvents and solutes.

Criteria of Purity:

Purity of the purified solvent and solutes was ascertained by measuring their physical constants such as m.p., b.p. and refractive index (n_D). The values observed are recorded in Tables II-1 and II.2.

Preparation of Solutions:

For the determination of dipole moment in ground state the solutions of desired weight fractions (W_2) were prepared in a specially designed ground glass stoppered flask to minimise error in weighing due to evaporation of solvent.

For the spectroscopic measurements, generally a stock solution of concentration 1 x 10^{-3}M was first prepared, the solution of desired concentration being then obtained by successive dilutions. Diluteions were carried out with calibrated 1 and 2 ml. graduated pipettes and 5,10 ml specially designed ground glass-stoppered volumetric flasks. All the weighings for spectroscopic measurements were done on a microchemical balance, weighing accurately up to 0.001 mg.

II. B Experimental Cell and Determination of Dielectric Constant, Density and Refractive Index:

Experimental Cell :

A special type of experimental cell Fig. II.1 was designed so as to avoid contamination of moisture with solution under investigation and carry out the measurement in an absolutely dry atmosphere. It consisted of two concentric stainless steel cylinders held rigidly by means of properly ground teflon spacers. The inner one was solid cylinder so as to avoid an excess of the solution. It was connected to H.T., while the outer one was earthed. The cell was placed in a glass container with a B 34 ground glass lid. The leads of the respective cylinders were sealed in the B 34 ground glass lid of the container using araldite adhesive so that when properly placed, the entire assemble was perfectly air tight. The cell could be evacuated by connecting end A of the lid to vacuum pump and fresh dry air was allowed to enter tne cell through end B.

The cell container was fitted in an outer glass jacket provided with an inlet and outlet for circulating thermostate liquid. A thermometer with 0.1 degree accuracy was fitted at the outlet of the jacket so that the temperature of the out going thermostated liquid could be determined. The desired temperature ($30^{o}C$) was maintained by using MLW, thermostat U10 (GDR).

Measurement of capacitance:

The present work deals with the determination of dielectric constant by the electrical capacitance measurement method. The following three methods [12] have been reported for the determination of electrical capacitance.

Table - II.1 : Physical Constants of the solvents:

Sr. No.	Solvent (cut off/nm)	Boiling point t /°C		Density $d^{t^{\circ}C}/g\ cm^{-3}$		Dielectric constant $D^{25^{\circ}}$		Refractive index $n_D^{25^{\circ}}$		Ref. for lit. value
1.	n-Pentane	36.3	(a)					1.35454	(a)	9,10
	(210)	36.7	(b)	0.62139^{25}	(b)	1.844^{20}	(b)	1.35472	(b)	
2.	n-Hexane	68.4	(a)					1.37230	(a)	9
	(210)	68.7	(b)	0.65482^{25}	(b)	1.883	(b)	1.37226	(b)	
3.	iso-Octane	98.9	(a)					1.38870	(a)	9
	(210)	99.2	(b)	0.68681^{25}	(b)	1.933	(b)	1.38898	(b)	
4.	Cyclohexane	80.5	(a)					1,423506	(a)	9
	(210)	80.7	(b)	0.76928^{30}	(b)	2.015	(b)	1.42354	(b)	
5.	Diethyl ether	34.4	(a)					1.3494	(a)	1,9
	(220)	34.6	(b)	0.708^{25}	(b)	4.335	(b)	1.3497	(b)	
6.	Acetonitrile	81.4	(a)					1.34159	(a)	1,9
	(210)	81.6	(b)	0.77683^{25}	(b)	37.50	(b)	1.34163	(b)	

CONTD.

Table - II.1. (contd.)

Sr. No.	Solvent (cut off/nm)	Boiling point t / ^{o}C	Density $d^{t^{o}C}/g\ cm^{-3}$	Dielectric constant $D^{25^{o}}$	Refractive index $n_D^{25^{o}}$	Ref. for lit. value
7.	Benzene	79.9 (a)	0.8736^{25} (a)	-	1.49754 (a)	1,9
		80.1 (b)	0.8737^{25} (b)	2.274 (b)	1.49790 (b)	
8.	Dioxane	101.0 (a)	1.0263^{25} (a)	2.2365 (a)	1.42018 (a)	1
		101.3 (b)	1.02687^{25} (b)	2.209 (b)	1.42025 (b)	

(a) Present work, (b) Literature value.

Table - II.2 : Physical constants of the solute :

Sr. No.	Substance	Boiling point/ melting point t /°C	Density d^{25°/g cm^{-3}	Refractive index $n_D^{25^\circ}$	Molecular volume/ A^{o3}	Cavity radius a_o/ Å	Ref. for lit. value
1.	Benzaldehyde	178.8 (a)	1.0433 (a)	1.54274 (a)	16.7 (a)	1.59 (a)	1
		179 (b)	1.0434 (b)	1.54290 (b)	—	—	
2.	2-Methoxy-benzaldehyde	36.8°C(a)	—	—	32.632 (a)	1.982 (a)	23
		37.8°C(b)	1.1326_4^{20} (b)	1.5600^{20}(b)	-	-	
3.	3-Methoxy-benzaldehyde	230°C (a)	—	—	32.632 (a)	1.982 (a)	23
		230 (b)	1.1187_4^{20} (b)	1.5530^{20} (b)	—	—	
4.	4-Methoxybenzaldehyde	249.3 (a)	—	—	29.447 (a)	1.915 (a)	23
		249.5 (b)	1.1191_4^{15} (b)	1.5730^{20}(b)	—	—	

(a) Present work (b) Literature Value.

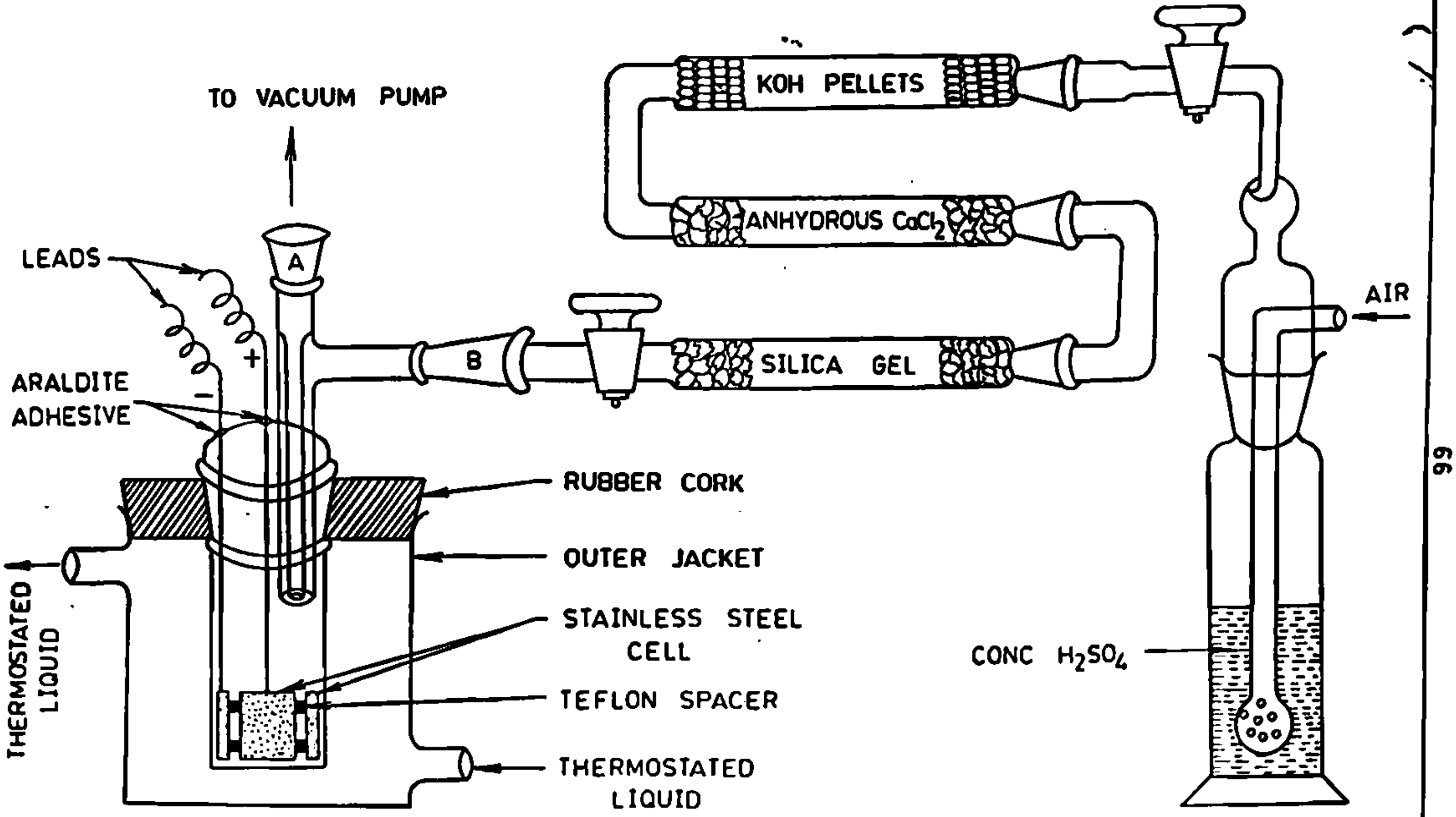

FIGURE II.1 - EXPERIMENTAL CELL WITH DRYING ASSEMBLY

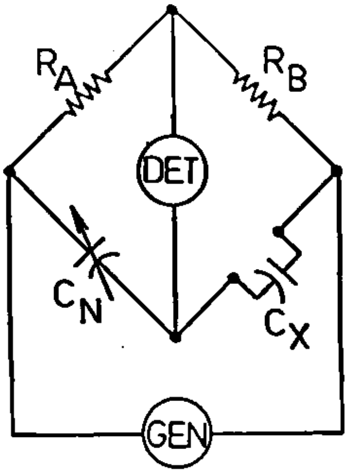

Fig. II . 2a. Basic ratio bridge

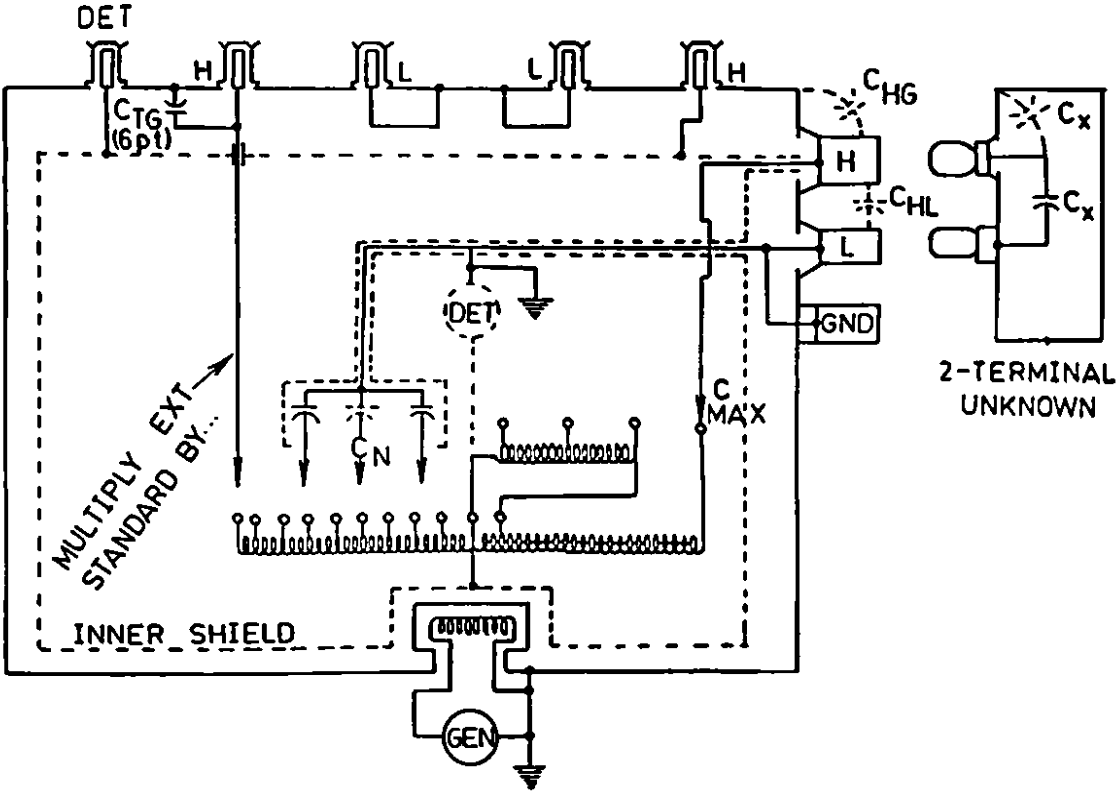

Fig. II. 2b. : Bridge circuit for 2-terminal capacitance measurement.

i) Capacity bridge method
ii) Resonance method
iii) Heterodyne beat method

In the present work, capacity bridge method was employed; using type 1620-AP capacitance measuring assembly of General Radio Company, USA. The capacitance measuring assembly for the precise measurement of capacitance consisted of the following units.

i) Capacitance bridge (type 1615-A)
ii) Audio oscillator (Type 1311-A)
iii) Tuned amplifier and null detector (type 1232-A).

The fixed frequency of 1000 cps and capacitance bridge for two-terminal capacitance measurement were employed in the persent work for which the circuit diagrams are shown in Fig. II.2a and II.2b .

Determination of Lead Correction :

The cell was cleaned repeatedly with alcohol and acetone. It was then dried by passing a stream of hot air which was followed by evacuation of cell at 40°C, using a vacuum pump. Fresh dry air was then introduced into the cell by passing atmospheric air through the drying assembly (Fig. II.1). The dielectric constant (D) of a solution may be calculated by using the expression[13],

$$D = \frac{C_L - a}{C_A - a} \qquad \text{.. .. (II.1)}$$

where C_L = the capacity of the cell filled with liquid,

C_A = the capacity of the cell with air, and

a = the lead correction.

The capacity of cell with air and benzene were determined at 25°C and 30°C. The lead corrections 'a' at these temperatures were calculated, using the literature value[9] of dielectric constants of benzene at these temperatures.

Determination of Dielectric Constant:

After all the preliminary operations mentioned earlier, the measured volume of the solution of known weight fraction was introduced into the cell and the capacity of the cell was measured at the desired temperature. Knowing a, C_L and C_A at the corresponding temperature, the dielectric constant of the solution was calculated by using Eq. II.1.

Measurement of Density:

Weissberger[14] has reported various convenient methods for determination of density. Lipkin's pycnometer[15,16] of 0.5 min diameter capillary was employed in the present work.

The level of liquids in the two arms above the reference mark was more accurately measured with a travelling microscope reading to ± 0.001 cm. It was calibrated with double distilled water at different temperatures[17] in a thermostat controlled to ± 0.01 °C. All weighings were accurate to ± 0.00001 g and the density value better than ± 0.0001.

Measurement of Refractive Index:

The refractive indices at 25°C and 30°C were determined using Abbe refractometer at the wavelength of sodium D line ($\lambda = 5893\ A^{o}$).

II. C Spectroscopic Measurements:

The electronic absorption spectra of the various compounds were recorded on microprocessor controlled Hitachi (200 A) double beam UV-Visible spectrophotometer using a pair of matched 1 cm. quartz cells, with settings (1) slit width= 1nm, (2) absorbance range = 0 to 1 (3) scan speed 60 nm/ minute, (4) response time 0.1 sec, and (5) wavelength scale= 5 to 10 nm cm^{-1} were used. The measurements were carried out at room temperature in n-pentane, n-hexane, iso-octane and cyclohexane solvents within a concentration range 1×10^{-5} to 1×10^{-6} M against the same reference solvent. Bands with small values of molar absorptivity were obtained by selecting appropriate concentration of solution or with the help of the absorbance scale expansions.

The data obtained in nm on the positions of the maxima for the bands, λmax, were converted into the frequency scale by the relation $\bar{\nu}_s$ (cm^{-1}) = $10^7/\lambda$max. The molar absorptivity, ϵ, was calculated according to the formula : $\epsilon = \frac{A}{c.l}$ where c denotes the molarity of the solution, l the path in cm and A the absorbance. The approximate oscillator strength 'f' was evaluated by using the formula :

$$f \simeq (4.6 \times 10^{-9}) \quad \epsilon_{max} \cdot \quad \Delta\bar{\nu}_{1/2}$$

where ϵ_{max} is the molar absorptivity at the λ_{max} and $\Delta\bar{\nu}_{1/2}$ the half band width of the corresponding band. The half-band width and the oscillator strength were calculated for the most intense local maxima of the transition.

The accuracy of wavelength measurement is better than ± 0.2 nm since the wavelength scale of the instrument is linear. The errors in the measurement of absolute molar absorptivities, which are essentially due to concentration errors, are probably less than 5 %. In some cases, it was not possible to determine precisely the absorptivities because of very low solubility of the solute.

II.D Methods for Computing Dipole Moment in Ground State:

The applications of various equations indicated minor differences in the observed values of dipole moments because of concentration, solute-solute and solute-solvent interactions which can be eliminated by using extrapolation methods like Halverstadt-Kumler[21], Guggenheim and modified Jatkar[22] equations. Hence we have used only Halverstadt-Kumler method and modified Jatkar methods for calculation.

1. Helverstadt-Kumler Method[21]:

When the concentration is expressed in weight fraction, following equations are used:

$$P_{2\infty} = \left[\frac{3\alpha V_1}{(D_1 + 2)^2} + \frac{D_1 - 1}{D_1 + 2} (V_1 + \beta) \right] M_2 \quad \text{(II.1)}$$

and

$$P_e = \left[\frac{3\gamma V_1}{(n_1^2 + 2)^2} + \frac{n_1^2 - 1}{n_1^2 + 2} (V_1 + \beta) \right] M_2 \quad \text{(II.2)}$$

where $P_{2\infty}$ is the molar polarization of solute at zero concentration, α, β and γ are the slopes and D_1, V_1 and n_1^2 are the ordinate intercepts of $D_{12} - W_2$; $V_{12} - W_2$ and $n_{12}^2 - W_2$ plots respectively. These values were computed by using the method of least squares.

The contribution due to the atomic polarization was taken as described earlier.

The orientation polarization of solute was then calculated by using the expression

$$P_o = P_{2\infty} - P_e - P_a$$

Finally dipole moment (μ_g) of the solute was calculated by the formula

$$P_o = \frac{4\pi N \mu_g^2}{9\,kT} \qquad \cdots \quad \cdots \qquad (II.3)$$

2. Modified Jatkar Equation[22]

For the concentration in weight fraction

$$P_{2\infty} = \left[\alpha V_1 + (D_1 - 1)\;(V_1 + \beta) \right] M_2 \qquad \cdots \qquad (II.4)$$

and

$$P_e = \left[\gamma V_1 + (n_1^2 - 1)\;(V_1 + \beta) \right] M_2 \cdots \qquad (II.5)$$

The terms involved in the above two expressions have the same significance as mentioned in Halverstadt-Kumler equation.

The contribution due to the atomic polarization was taken as described earlier.

The orientation polarization and hence the dipole moment (μ_g) was calculated by using the following relation:

$$P_o = P_{2\infty} - P_e - P_a = \frac{4\pi N\mu^2_g}{3KT} (0.8955 D_1) \quad (II.6)$$

II.E Determination of Solvatochromic Shifts and Dipole Moment in Excited State:

In view of the practical utility of estimating excited state dipole moments, the method has been modified[18] by logical and systematic steps as given below:

(1) The solvent for such measurements must be restricted to saturated hydrocarbons like pentane, hexane, heptane, octane, cyclohexane etc. which are the least reactive solvents. The solute-solvent interactions in such solvents would then be very similar in nature, the magnitude depending mostly on their dielectric constants as implied in the dielectric model under consideration. Thus, in the present work, only the saturated hydrocarbon solvents (n-pentane, n-hexane, iso-octane and cyclohexane) were employed in the determination of μ_e and $\Delta\mu_{e,g}$.

(2) The subjectivity in the choice of the reference solvent and thereby in $\Delta\bar{\nu}$ can be removed by measuring the frequency $\bar{\nu}_v$ of the band corresponding to an isolated solute molecule.

The $\Delta\bar{\nu}$ so determined is the better measure of the solute-solvent interaction. If experimental vapour phase frequencies ($\bar{\nu}_v$) are not available, as is generally the case, then considering vacuum as the reference solvent ($D = n^2 = 1$) the equations I.19, I.20 and I. 24 can be written as

$$\bar{\nu}_s = \bar{\nu}_v - \left[(A+A') + \frac{\mu_e^2 - \mu_g^2}{hca_o^3} \right] \frac{n^2-1}{2n^2+1} \qquad ..(II.7)$$

$$\bar{\nu}_s = \bar{\nu}_v - \left[\frac{\mu_e^2 - \mu_g^2}{hca_o^3} \right] \frac{2(n^2-1)}{2n^2+1} \qquad ..(II.8)$$

and

$$\bar{\nu}_s = \bar{\nu}_v - \left[\frac{\mu_g \cdot \Delta\mu_{e \cdot g}}{hca_o^3} \right] \frac{2(D-1)}{2D+1} \qquad ..(II.9)$$

respectively, where the subscripts v and s refer the vacuum and particular solvent respectively. Now the $\bar{\nu}_s$ values can directly be plotted as a function of $\frac{n^2-1}{2n^2+1}$ or $\frac{2(n^2-1)}{2n^2+1}$ or $\frac{2(D-1)}{2D+1}$ yielding μ_e or $\Delta\mu_{e,g}$ from the slope as expected. In case of McRae's equation[14] contribution of $(A+A')$ to the slope is very small and can be neglected. Because of restricting the solvents to hydrocarbon class, the slope of the present line would be physically more meaningful. In addition, the inrecept of the straight line on the frequency axis gives the vapour phase frequecy $\bar{\nu}_v$. Such an extrapolation would not be meaningful when all kinds of solvents are incorporated in one and the same graph.

In the present work, Eqs. II.7-9 were utilized in the determination of μ_e and $\Delta\mu_{e,g}$ values. In the similar way, the following equation

$$\bar{\nu}_s = \bar{\nu}_v - \left[\frac{\mu_g - \Delta\mu_{e,g}}{hca_o^3} \right] \frac{2(D-1)}{D+2} \quad .. \text{(II.10)}$$

was also employed to obtain $\Delta\dot{\mu}_{e,g}$ values [18b].

Various functions of D and n used in the determination of μ_e and $\Delta\mu_{e,g}$ values are listed in the following table. In this calculation, the values of D and n have been taken from Table II.1.

Table : II.3 : Functions of D and n corresponding to various solvents

Solvent	$\frac{n^2-1}{2n^2+1}$	$\frac{2(n^2-1)}{2n^2+1}$	$\frac{2(D-1)}{2D+1}$	$\frac{2(D-1)}{D+2}$
n-Pentane	0.17876	0.35753	0.3601	0.4391
n-Hexane	0.18530	0.37060	0.3724	0.4576
iso-Octane	0.19113	0.38226	0.3852	0.4772
Cyclohexane	0.20313	0.40626	0.4055	0.5086
Diethyl ether	-	-	-	1.0529
Acetonitrile	-	-	-	1.8481

(3) A proper measure of the cavity size will be the volume of a single solute molecule calculated from its bond lengths and angles, considering the molecule as an ellipsoid which is a better approximation than the spherical or cylindrical shape. The lengths of the ellipsoid axes (A, B and C) were determined by projections of various bonds in three mutually perpendicular directions (a, b and c) which are more or less obvious from the molecular skeleton. Equating the ellipsoid volume ($V = \frac{4}{3}\pi \frac{A}{2}\cdot\frac{B}{2}\cdot\frac{C}{2}$) with that of an equivalent spherical cavity ($V = \frac{4}{3}\pi a_o^3$) gives $a_o = 3\sqrt{ABC/2}$. If some groups in the solute molecule are capable of free rotation, the ellipsoid axes were appropriately averaged out over possible conformations.

The following example of benzaldehyde will illustrate the approach wherein bond lengths and bond angles are required for the calculation. These parameters[19,20] are listed in Fig. II.3 .

A = $\sum$ projections of bonds on a-axis
= 4.29 Å

B = $\sum$ projections of bonds on b-axis
= 5.93 Å

C = $\sum$ projections of bonds on c-axis
= 1.97 Å

Projection of -CHO group on c-axis changes from minimum 0 to maximum c when θ changes from 0 to $\pi/2$ as a result of the rotation of the group about C_1-C axis where θ is an angle between the planes of the aromatic nucleus and the -CHO group. Therefore the calculation of an average value (C_{avr}) of all projections on c-axis is required. Evaluation of C_{avr} is carried out in the following way,

$$C_{avr} = \sum_{\theta=0}^{\pi/2} c \sin \theta \;/\; \pi/2$$

or

$$= \int_{0}^{\pi/2} c \sin d\,\theta \;/\; \pi/2$$

where c sin θ is the projection of the - CHO group on C-axis at any moment corresponding to the angle θ . After solving the integration the value of $C_{avr} = 0.6364$ C is obtained.

$\therefore$ Volume of the molecule

$$= \frac{4}{3}\pi \frac{A}{2} \frac{B}{2} \cdot \frac{0.6364\ C}{2}$$

$$= 16.70\ \text{Å} .$$

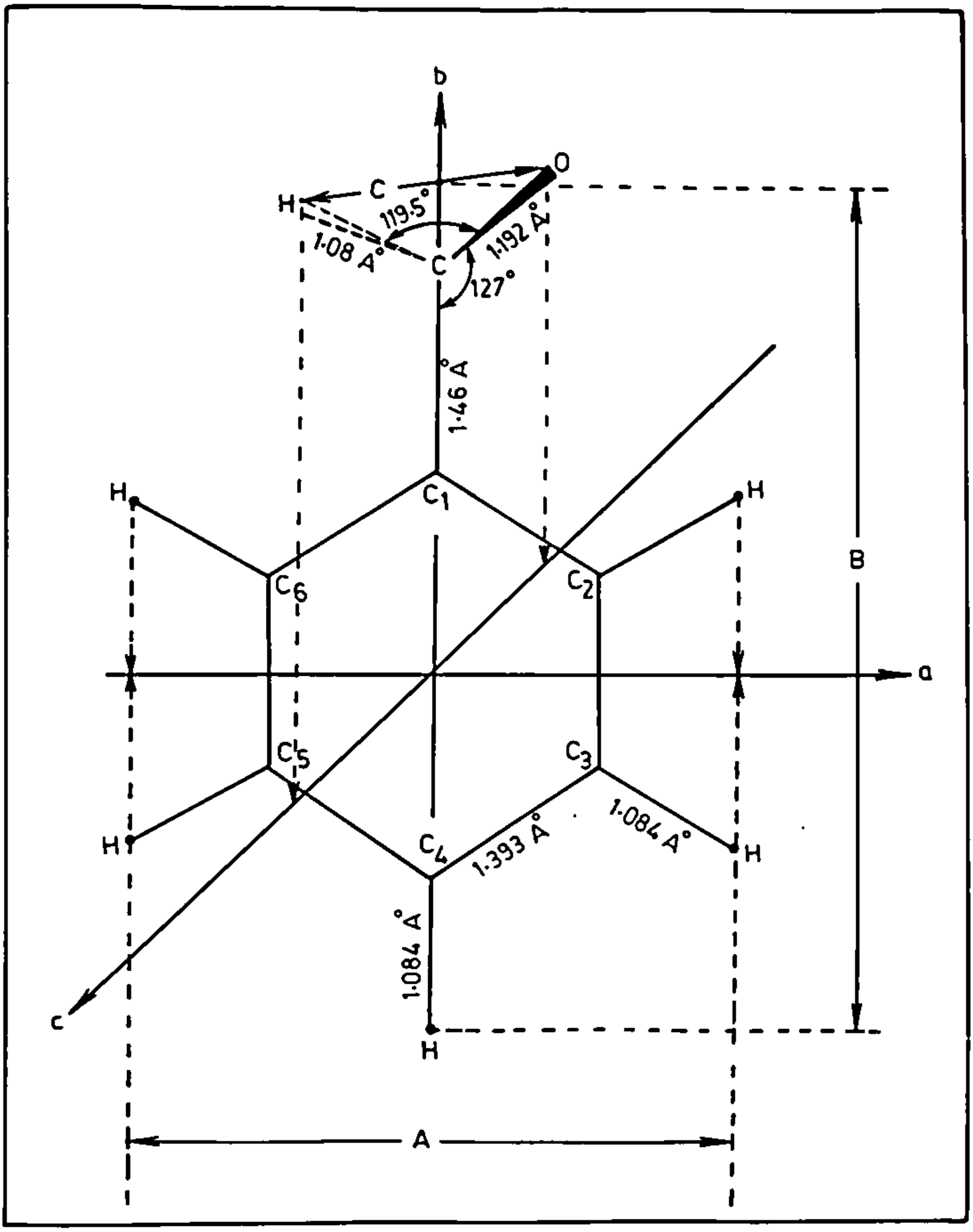

Fig II.3 : Determination of length of ellipsoid axes A, B and C for Benzaldehyde from molecular skeleton.

Equating the ellipsoid volume with that of an equivalent spherical cavity ($\frac{4}{3}\pi a_o^3$), the value of the cavity a_o is obtained as 1.59 Å .

A BASIC Computer program was written for the calculations, BBC microcomputer was used.

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* * *

CHAPTER - III

CHAPTER III

ANISALDEHYDES : A STRUCTURAL PERSPECTIVE

A large experimental data is published related to the anisaldehyde isomers, specially as vital reactants and intermediates; accordingly its structure is also predicted. We feel that a natural continuity flows in the interaction of these molecules to various parts of the energy spectrum and such understanding is possible if the basic electrical nature of matter is taken into account. From this point of view, the basic electrical entity, the dipole moment of these molecule is studied both in ground and excited state and a correlation of these values is sought with ^{13}C NMR and the UV spectrum of these compounds.

CHAPTER III-A

DIPOLE MOMENTS OF ANISALDEHYDES IN THE GROUND STATE

III.A.1 : Results and Discussion

The experimental data of dielectric constant, density and refractive index of isomers of anisaldehydes at various concentrations in the solvent benzene at 30 °C have been listed in Tables III.1 - III.3. The molar polarization values $P_{2(\infty)}$ at infinite dilution, calculated from modified Jatkar (MJ)[1] and Halverstadt-Kumler method (HK)[2] and the corresponding dipole moment values from these equations are listed in the last two columns of these tables. The sum of the electronic and atomic polarization values $P_{(e+a)}$ are given at the top of each table for modified Jatkar equation and Halverstadt-Kumler (HK) method. For the interpretation of results, dipole moment value obtained by Halverstadt-Kumler method at 30 °C have been used. The values of dipole moments investigated in the present works along with the available literature values are given in Table III.4 for comparison.

Table III.1

Dipole moment of 2-methoxybenzaldehyde at 30 °C

Solvent	$P_{(e+a)}$ (MJ) (cm^3)	$P_{(e+a)}$ (HK) (cm^3)
Benzene	169.61	38.51

$W_2 \times 10^2$	D_{12}	d_{12} ($gm.cm^{-3}$)	n_{12}	Slopes	$P_{2\infty}$ (cm^3)	μ_g(D)
0.0000	2.265	0.86844	1.4947	α=15.022	MJ= 2506.06	4.270
0.97384	2.406	0.86985	1.49494	β=-0.2750	HK= 423.80	4.377
2.02694	2.562	0.87206	1.49544	γ= 0.1425		
2.99128	2.694	0.87411	1.49595			
3.72969	2.813	0.87573	1.49626			
4.68445	2.967	0.87760	1.49670			

Table III.2

Dipole moment of 3-methoxybenzaldehyde at 30 °C

Solvent	$P_{(e+a)}(MJ)$ (cm^3)	$P_{(e+a)}(HK)$ (cm^3)
Benzene	161.24	37.873

$W_2 \times 10^2$	D_{12}	d_{12} ($gm.cm^{-3}$)	n_{12}	Slopes	$P_{2\infty}$ (cm^3)	$\mu_g(D)$
0.0000	2.265	0.86844	1.4947	α=6.8294	MJ = 1232.84	2.959
0.87136	2.330	0.87040	1.49515	β=-0.2098	HK = 214.60	2.965
1.66745	2.388	0.87168	1.49521	γ=0.01935		
2.4364	2.441	0.87297	1.49526			
3.24006	2.495	0.87414	1.49531			
3.9649	2.541	0.87538	1.49535			

Table III.3

Dipole moment of 4-methoxybenzaldehyde at 30 °C

Solvent	$P_{(e+a)}^{(MJ)}$ (cm^3)	$P_{(e+a)}^{(HK)}$ (cm^3)
Benzene	157.74	36.74

W_2x 10^2	D_{12}	d_{12} (gm.cm^{-3})	n_{12}	Slopes	$P_{2\,\infty}$	μ_g(D)
0.000	2.265	0.86844	1.4947	α=13.072	MJ = 2203.47	4.0894
0.8023	2.351	0.86995	1.49532	β=-0.2567	HK = 374.12	4.0966
1.6788	2.450	0.87171	1.49546	γ=0.0472		
2.4412	2.553	0.87305	1.49557			
3.2149	2.643	0.87459	1.49571			
4.0131	2.775	0.87630	1.49582			

Table III.4

Summary of dipole moments of isomeric methoxybenzaldehydes(MBH)

Compound	Solvent	μ_g(D) at 30 °C present work	Literature value of μ_g(D)		Reference
			at 20°C	at 25°C	
2-Methoxybenzaldehyde	Benzene	4.37	4.19	4.24	16, 17
3-Methoxybenzaldehyde	Benzene	2.96	-	2.90	18
4-Methoxybenzaldehyde	Benzene	4.09	3.8	3.9	18, 19

III.A.2 : Vectorial addition method for Estimating μ_g, calculated

The use of the dipole moment value of a molecule to investigate its structure, involves comparison of the experimental value of the moment with the one, calculated by the additive method, based on the rules of vector algebra. To calculate the expected moment (μ_g, calc.) of substituted benzene derivatives, the concept of group moment is very useful. Using the value of θ (the angle of orientation of the dipole moment vector) as 146° and 72 °C for -CHO and $-OCH_3$ group respectively and assuming the magnitudes of -CHO and $-OCH_3$ group moments as 2.95 D and 1.21 D respectively[3], the expected dipole moments (μ_g, calc.) have been calculated for the methoxybenzaldehyde isomers.

III.A.3 : Illustrative Calculation[3]

The method consists of projecting the vector of dipole moment μ on arbitrarily chosen coordinate axes and evaluating the components m_x, m_y and m_z. Results is expressed as

$$\mu = (m_x^2 + m_y^2 + m_z^2)^{1/2}$$

If a molecule contains n polar groups, corresponding appropriate formula is

$$\mu = \left[\left(\sum_{i=1}^{n} m_{xi} \right)^2 + \left(\sum_{i=1}^{n} m_{yi} \right)^2 + \left(\sum_{i=1}^{n} m_{zi} \right)^2 \right]^{1/2}$$

In order to calculate the projections, one must know the angles between the vectors of group moments and the coordinate axes. In some cases, particularly for planar molecules, these angles are easy to calculate when the valence angles are known.

Illustrative calculation in this respect is given below in the case of two probable conformers of para-anisaldehyde.

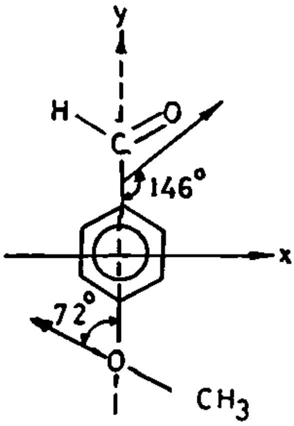
The values of structure (I) (Fig. III.1A) and structure (II) (Fig. III.1B) are reported in corresponding Tables III.5 and III.6.

The calculated dipole moment values of two conformers are 2.88 D (Structure I) and 4.04 D (Structure II). The root mean square value can be estimated as follows.[3]

$$\begin{aligned}\mu^2 &= \sum_{i=1}^{n} N_i \mu_i^2 \\ &= \frac{1}{2}(2.88)^2 + \frac{1}{2}(4.04)^2 \\ \mu_{RMS} &= 3.51\ \text{D}.\end{aligned}$$

If this value is very close to the experimental value then we conclude that conformers I and II exist in equal proportion in the equilibrium mixture.

Similar calculations are made for each of the probable conformers of methoxybenzaldehydes. The values thus obtained are mentioned in the subsequent discussion.



(I)

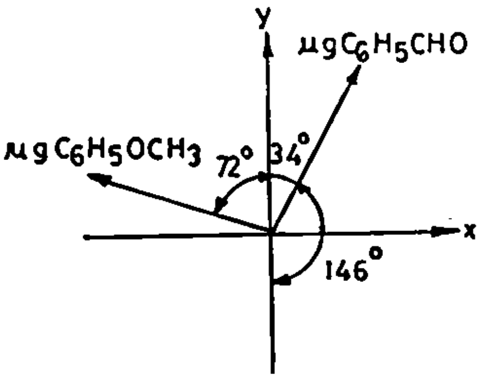


Fig. III.1A

Table III.5

Projection of group moments of -CHO and $-OCH_3$ on x and y coordinates.

Group	mx	my
-CHO	2.96 sin 34 = + 1.655	2.96 cos 34 = + 2.45
$-OCH_3$	-1.28 sin 72 = - 1.217	+1.28 cos 72 = + 0.395
	Σm_{xi} = 0.438	Σm_{yi} = 2.845

$$\mu_{calc} = \left[(\Sigma m_{xi})^2 + (\Sigma m_{yi})^2\right]^{1/2}$$

$$= 2.88 \text{ D}$$

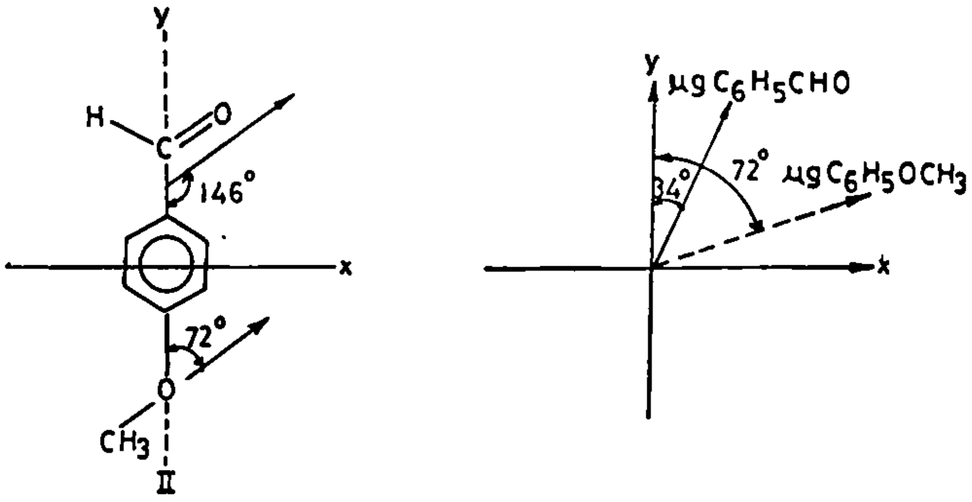


Fig. III. 1B

Table III.6

Projection of group moments of $-CHO$ and $-OCH_3$ on x and y coordinates.

Group	m_x	m_y
$-CHO$	2.96 sin 34 = + 1.655	2.96 cos 34 = + 2.45
$-OCH_3$	1.28 sin 72 = - 1.217	1.28 cos 72 = + 0.395
	Σm_{xi} = 2.872	Σm_{yi} = 2.845

$$\mu_{calc.} = \left[(\Sigma m_{xi})^2 + (\Sigma m_{yi})^2 \right]^{1/2}$$

$$= 4.04 \text{ D.}$$

III.A.4 : Stereochemistry of anisaldehyde isomers

One should take into account following facts while proposing the stereochemistry of various anisaldehyde isomers.

(1) The group moment and the angle of orientation of the groups[3] are

$-CHO$ (μ_g = 2.96 D; θ = 146°) and

$-OCH_3$ (μ_g = 1.28 D; θ = 72°).

(2) (a) The steric factor

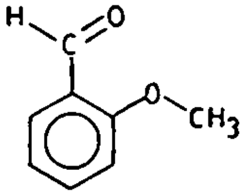
(b) The conjugation with the aromatic ring and

(c) The electrostatic forces

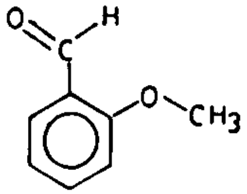
considered together

For example, in o-anisaldehyde, steric crowding between the ortho groups, $-CHO$ and $-OCH_3$, tends to push them out of the plane of the aromatic ring, while the mesomeric effect favours the planar conformation of these groups so as to have effective conjugation with the ring and also with each other through the ring. The very fact that both $-CHO$ and $-OCH_3$ groups of anisaldehyde are in the same plane[5] of aromatic ring itself reveals that the conjugation effect dominates the steric factor in this case.

The electrostatic factor also affects the relative stability of the conformers. Thus, in prediction of the relative abundance of the isomers present in the equilibrium mixture of o-anisaldehyde,


(I)

$\mu_{cal} = 3\cdot93\,D$


(II)

$\mu_{cal} = 4\cdot2\,D$

the conformer I in which the positively charged ether oxygen is closer to the carbonyl group, should predominate[6] in the equilibrium mixture.

Such prediction should be supported by other evidences; e.g. the local variation of electron density as reflected in NMR shift. Delocalization of electron density can also be predicted by the molar extinction coefficient in the u.v. spectrum.[7]

Using above general principles and the data collected experimentally or from literature, we propose following analysis of the structures of anisaldehyde isomers.

III.A.5 : Stereochemistry of o-anisaldehyde

The nearly planer structure of this molecule is first evidenced by the high molar extinction coefficient (Table III.7) of the $\pi - \pi^*$ band. The easy electron delocalization is facilitated only when p orbitals of benzene nuclei and the resonating substituent groups are overlapping and are parallel to each other. This condition is possible only in a planer conformation. Thus the planer conformation reflects in high molar extinction coefficient.

The second evidence can be located in ^{13}C NMR spectrum of the compound.[14] Lauterber[8,9] has demonstrated that there exists an 'additive' relationship for the effect of substituents on aryl carbon shielding in a number of benzene derivatives. Since the chemical shifts for the aromatic carbons in several monosubstituted benzenes have been reported by Spiesecke and Schneider[10], it is possible to predict the shieldings in other derivatives by using these data and assuming additivity. In general, in ortho substituted anisoles this additivity is disturbed.[11,12,13] The magnitude of the deviation from this additivity is a crude measure of steric hindrance to the electronic interaction and resonance of methoxyl function.

The methoxyl and aryl carbon shieldings in anisaldehydes are reported by Stothers and Dhami[14] as

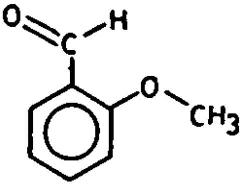
Table III.7

^{13}C shieldings of methoxyl and aryl carbon nuclei in some substituted anisoles (in ppm from CS_2)[14]

Substituent	Methoxyl Carbon	Aromatic carbons					
		C-1	C-2	C-3	C-4	C-5	C-6
2-CHO	138.8	32.9	70.3	66.7	73.9	58.2	82.5
4-CHO	137.6	29.0	79.2	63.2	63.5	63.2	79.2
anisole	138.8	32.8	78.6	63.1	72.2	63.1	78.6

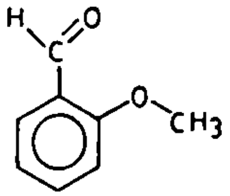
These values can be compared with those predicted by additivity.

The methoxyl group has marked deshielding effect on C-1. For 2-formyl anisole (o-anisaldehyde), it seems probable that the preferred planer conformation will be that in which the carbonyl oxygen and methoxyl methyl group are as far apart as possible.



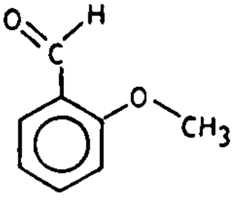
This probability stems up from C-6 shielding which differs by 3.9 ppm from C-6 shielding in anisole (in p-anisaldehyde the deviation is only 0.6 ppm). This suggests that C-6 shift to higher fields is caused by location of the methoxyl carbon. If a planer conformation is assumed, the distance separating the methoxyl and C-6 carbon nuclei is approximately the same as that between two ortho-oriented methyl groups on an aromatic ring.[14] For o-xylene it is well established that these nuclei are abnormally shielded.(8,11-13,15) This suggests the common origin for high C-6 shielding.

Thus taking planarity into consideration following two planer structures can be proposed along with the calculated dipole moment values.



(I)

$\mu_{cal} = 3 \cdot 93$ D



(II)

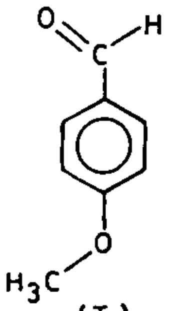
$\mu_{cal} = 4 \cdot 2$D

Although the structure I should be electrostatically stable, the evidence of ^{13}C NMR prefers structure II and our experimental value of the dipole moment, though slightly higher, confirms the same.

III.A.6 : Stereochemistry of p-anisaldehyde

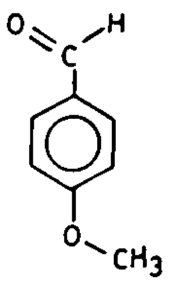
As discussed earlier, the high values of ϵ_{max} (Table III.11) are suggesting planer structure of the molecule.

^{13}C NMR (Table III.7) of anisole indicates highly shielded o- and p- positions i.e. high electron density at these positions. Now if an electron withdrawing group like -CHO or -COOH, bearing a carbonyl function, is attached at such a shielded position, then this density is easily shifted on to the carbonyl oxygen. The methoxyl carbon deshielding observed in anisole is almost the same as in p-anisaldehyde hence the electron withdrawing group must be deshielding the methoxyl oxygen along with methoxyl carbon. This suggests that mesomerism and conjugation is prominent in p-anisaldehyde, indicative of effective π overlap. Thus the following planer structures are proposed along with the vectorial moment values.



(I)

$\mu_{cal} = 2\cdot88D$



(II)

$\mu_{cal} = 4\cdot04D$

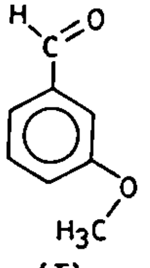
The experimental dipole moment value 4.09 D clearly indicates the dominance of structure II in the equilibrium mixture.

The justification of such dominance could perhaps be found in the symmetry consideration. The line passing through methoxyl 'O' and carbonyl 'C' has same mass on both sides only in structure II.

III.A.7 : <u>Stereochemistry of m-anisaldehyde</u>

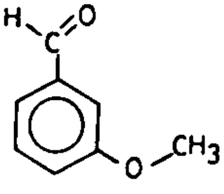
In this case also the high ϵ_{max} values are indicating the planarity of the molecule.

Dhami and Stothers[14] confirm that the Lauterber's[8(b)] additivity rule is observed in m-anisaldehyde and the shift-values of C-2 and C-4 confirm the orientation of methoxyl group in the same plane of aromatic ring. Thus the planarity of m-anisaldehyde can be assumed and following structures with vectorial moment values can be proposed.



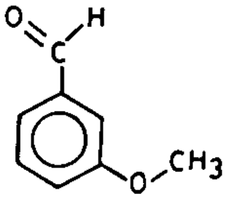
(I)

$\mu_{cal}=4{\cdot}17\,D$



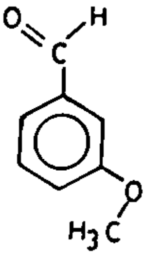
(II)

$\mu_{cal}=1{\cdot}74$



(III)

$\mu_{cal}=3{\cdot}05$



(IV)

$\mu_{cal}=3{\cdot}96$

As in the case of p-anisaldehyde, the consideration of symmetry about C_1-C_4 divider line suggests that structure III and IV are more probable. The experimental value of dipole moment suggests that structure III is the most probable structure.

CHAPTER III-B

SOLVENT EFFECT ON ELECTRONIC ABSORPTION SPECTRA AND DIPOLE MOMENT IN EXCITED STATE OF ANISALDEHYDES

The small shift in the frequency of absorption maxima of compound in UV spectrum, upon solvating the absorbing species, is apparently insignificant phenomenon but a wealth of information can be churned out of it. A redistribution of electron in the chromophore, upon excitation by an UV radiation, either increases or decreases its polarity and the dipole moment.

This information is made available upon estimating the dipole moment in excited state, by measuring the solvatochromatic shift.

The shift is also an indicator of the solute-solvent interaction energy, the polarity and solvating power of the solvent, the polarizability of solute and solvent molecules etc.

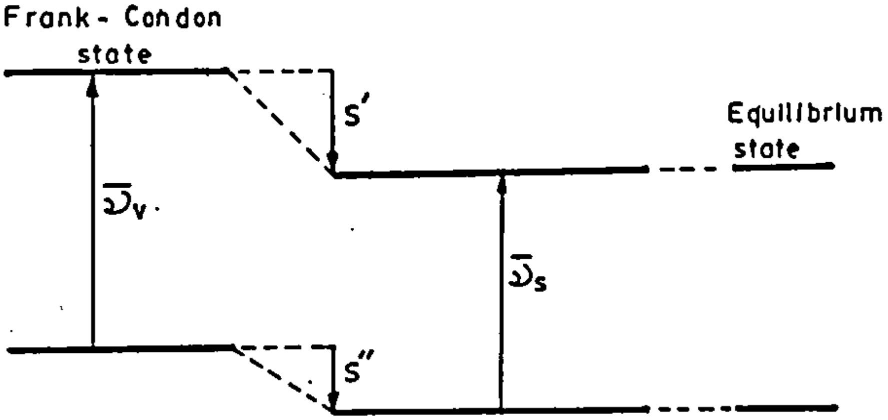


Fig.III-2 :The effect of solvation energies on the solution absorption frequency when dipole-polarization forces are dominant and when there is no orientation strain, i.e. when the Frank-Condon and equilibrium excited state have the same solvation energy. The solute dipole moment increases during the transition.

The knowledge is useful to understand the reactive centres of a photochemical reaction. The excited state dipole moments are also a valuable parameter in quantum mechanical calculations of various physico-chemical properties of molecules.

To evaluate this valuable parameter a study of solvatochromatic shifts is made of the anisaldehyde isomers, which is not reported in the literature.

The UV absorption spectra were recorded at room temperature, in solvents n-pentane, n-hexane, isooctane, and cyclohexane. The solutions ($\sim 1 \times 10^{-5}$ M) were prepared and then the absorption spectra were recorded. Usually the most intense local maxima of an electronic transition was considered to obtain the spectral characteristics such as the position of the maxima (λ_{max}) molar absorptivity (ϵ_{max}) half band width ($\Delta\bar{\nu}_{1/2}$) and oscillator strength (f). The cavity radii of the molecules were calculated from the molecular dimensions.

The equation given by McRae[20] and one that was further simplified by Suppan[21] were employed (Eqs. II.7-10) in the determination of the magnitudes of μ_e and $\Delta\mu_{e.g}$ The experimentally determined μ_g values calculated using HK [2] equation at 20 °C in benzene solution were utilized in the present work. The observations of solvatochromatic shifts, μ_e and $\Delta\mu_{e.g.}$ values were used to look into the changes in the electronic distribution in the excited state of the solute molecules.

McRae[20] has developed a general expression for the effect of solvents on the absorption frequency, in which he has considered the contribution from the dispersion forces between the solute and solvent molecules, interaction between the solute dipole and the induced-solvent dipole, interactions between the permanent dipoles of the solute and solvent and a term from the quadratic Stark effect. In practice many solute-solvent systems cannot be considered purely as a nonspecific interactions as mentioned above. In such cases, for example, the deviation from the $\bar{\nu}_s$ Vs $f(D)$ plot is often an indication that some specific interaction, usually much stronger than the dielectric stabilization, has occurred. This can be a complex formation in which one or more molecules of the solvent are bound strongly and specifically to the solute.

III.B.1 Determination of the cavity radius

The parameter a_o is the spherical cavity radius in the Onsagar[24] model, which is required in the calculation of μ_e. The method used for calculating a_o is already illustrated in Chapter II, wherein bond lengths and bond angles are required. The values of these bond and angle parameters[25,26] used for anisaldehyde are listed in Fig. II.3 and III.3.

Considering the ellipsoid form of the solute molecules, their molecular volumes and cavity radii have been computed. The calculated values of the length of ellipsoid axes (A, B and C), molecular volumes and cavity radius of the compounds are given in the Table III.8.

Table III.8 : Length of ellipsoid and (A,B,C) molecular volumes and cavity radii of anisaldehyde.

Molecule	A/A°	B/A°	C_{av}/A°	Mol.Vol / A^{o3}	Cavity* radii a_o
2-methoxy-benzaldehyde	6.63	5.93	1.585	32.632	1.982
3-methoxy-benzaldehyde	6.63	5.93	1.585	32.632	1.982
4-methoxy-benzaldehyde	4.29	8.27	1.585	29.447	1.915
Benzaldehyde	4.29	5.93	1.97	16.7	1.59

*Calculated a_o by projection.

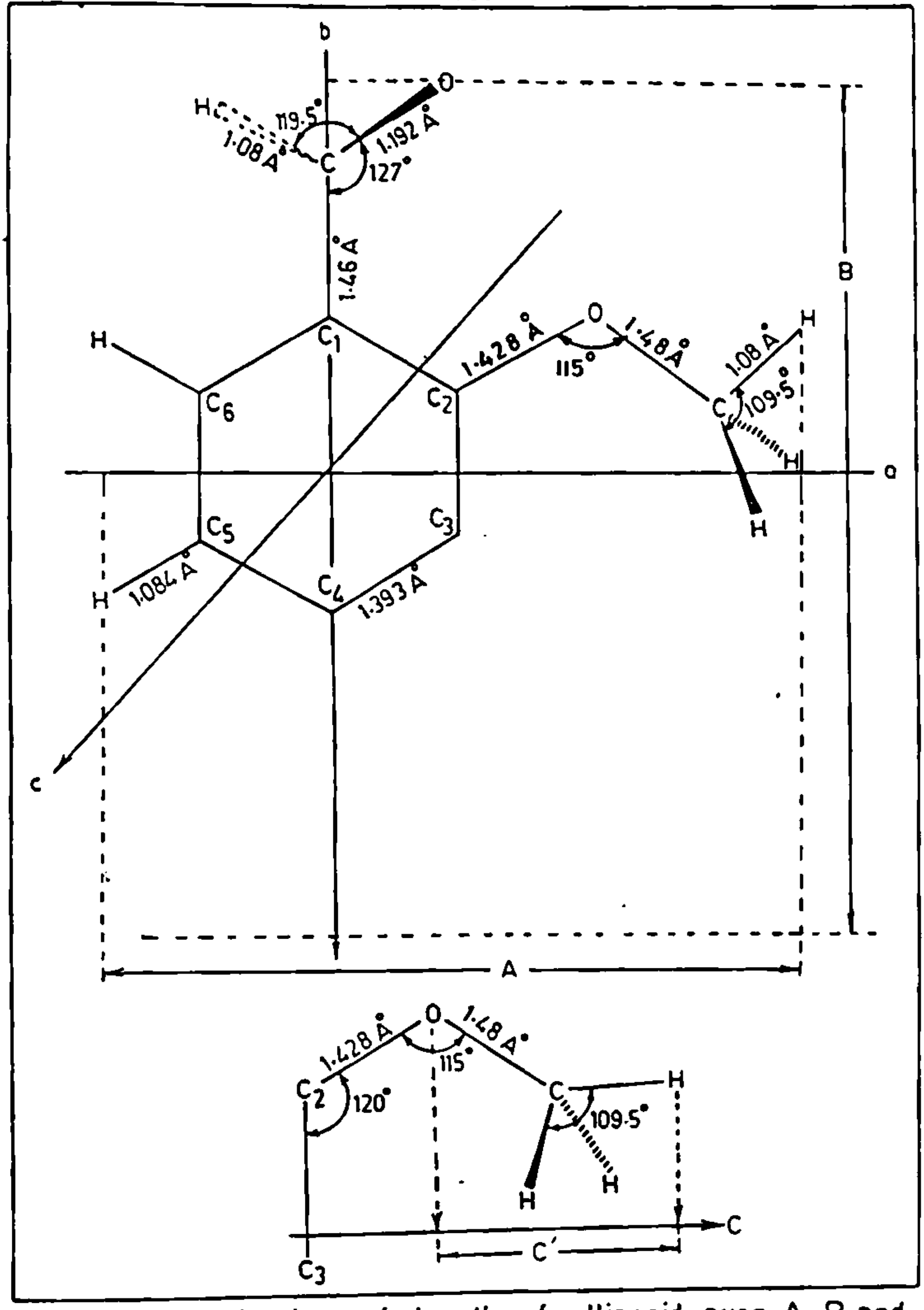


Fig.III-3: Determination of length of ellipsoid axes A, B and C for 2-methoxybenzaldehyde

III.B.2 : Determination of cavity radius a_o - modification

The method suggested to determine a_o by earlier workers[23,31] can not be the unique method. We propose here another approach to estimate a_o. The difference in the a_o values determined by these two methods naturally reflects in the μ_e value. Since there is no absolute measure for the value of the Onsager's cavity, such differences in the μ_e values are inevitable.

A look into basic concepts is useful. Lorentz-lorentz and Clausius Mossotti hypothesis assume polarization in the cavity field. Consequently polarization is proportional to the volume of the polarized cavity. The linear additivity of bond and atomic refractivities suggest that molar refractivity is a function of molar volume. Consequently, molar refraction very nearly represents the polarizable volume of the molecules. This is a fraction of the total molar volume m/d. Thus use of R to estimate a_o, the molecular radius offers a reasonable, polarizable volume. Onsager cavity envisages the same polarizable volume of the molecule, which by induced polarization creates the reaction field R. Hence an attempt is made to estimate a_o from R_D, which are listed in Table III.9. These values are more than the values calculated using bond lengths and bond angles

Table III.9 : Calculation of a_0 by molar refraction

Molecule	$P_{(e+a)}^{(HK)}$ (cm^3)	a_0/A°
2-methoxybenzaldehyde	38.57	2.094
3-methoxybenzaldehyde	37.87	2.083
4-methoxybenzaldehyde	36.74	2.062

in three dimension as depicted earlier. Also, these values are reasonably less than calculated from molar volume m/d. The values of μ_e calculated, therefore, appear to be more reasonable.

The values estimated with this modification are listed in Table III.10.

Table III.10

Compound	Slope 1	Intercept 1	Slope 2	Intercept 2	$\mu_{(g)}$/D	$\mu_{(E_1)}$ Sup	$\mu_{(E_2)}$ McRae
2-Methoxybenzaldehyde							
$a_{o(p)}$ = 1.982	-38840.70	42022	- 7768	42022	4.37	5.01	5.57
$a_{o(R_D)}$= 2.094	-38840.70	42022	- 7768	42022	4.37	5.11	5.76
3-Methoxybenzaldehyde							
$a_{o(p)}$ = 1.982	- 5340.44	42627	-10679	42626	2.96	4.11	5.01
$a_{o(R_D)}$= 2.083	- 5340.44	42627	-10679	42626	2.96	4.27	5.26
4-Methoxybenzaldehyde							
$a_{o(p)}$ = 1.915	- 1150.32	38076	- 2300	3807	4.09	4.28	4.46
$a_{o(R_D)}$= 2.062	- 1150.32	38076	- 2300	3807	4.09	4.23	4.55

$a_{o(p)}$ = Cavity radius by projection method

$a_{o(R_D)}$= Cavity radius by molar refraction.

Table III.11 : Frequencies ($\bar{\nu}$) of absorption band maxima corresponding molar absorptivities (ϵ_{max}), oscillator strengths (f) of methoxy benxaldehyde (MBH)

Compound	Solvent	Band	$\bar{\nu}_s$ / cm^{-1}	ϵ_{max}/ cm^{2}mol^{-1}	$\Delta\bar{\nu}_{1/2}$/ cm^{-1}	f
2-Methoxybenzaldehyde	a	K	40633.88	23783.00	3872.35	0.423
	b	K	40584.41	11621.90	4261.19	0.228
	c	K	40535.06	7063.24	3820.42	0.124
	d	K	40445.29	4443.58	1702.66	0.034
3-Methoxybenzaldehyde	a	K	40716.61	8704.71	3988.34	0.159
	b	K	40650.41	10382.10	4141.83	0.197
	c	K	40584.41	7328.46	4095.17	0.138
	d	K	40457.59	9113.37	1277.79	0.053
4-Methoxybenzaldehyde	a	K	37664.78	8620.00	2328.77	0.092
	b	K	37650.60	15399.35	2896.11	0.205
	c	K	37636.43	18521.99	4062.96	0.246
	d	K	37608.98	9058.00	4513.84	0.186

Contd ...

Table III.11 (Contd.)

Compound	Solvent	Band	$\bar{\nu}_s$ / cm^{-1}	ϵ_{max} / cm^{2}mol^{-1}	$\Delta\bar{\nu}_{1/2}$/ cm^{-1}	f
Benzaldehyde	a	B	35868	502	3124	0.007
	b	B	35862	468	2343	0.005
	c	B	35848	915	3831	0.016
	d	B	35778	348	3203	0.005
Benzaldehyde	a	K	41667	9215	8415	0.356
	b	K	41658	5879	4334	0.117
	c	K	41606	11044	4182	0.212
	d	K	41459	4004	4019	0.08

a = n-pentane
b = n-hexane
c = iso-octane
d = cyclohexane

III.B.3 : Results and Discussion

For convenience an abbreviation MBH is used in the following discussions for methoxybenzaldehyde(anisaldehyde)

Spectral features and assignments

The spectra of o-, m- and p-anisaldehyde in various solvents are depicted in Fig.III 4-III-9 . The bands around 245 nm (o- and m-anisaldehyde) and 265 nm (in p-anisaldehyde) are well isolated and suitable for recording the solvatochromatic shifts, hence these bands have been used for the purpose.

Benzaldehyde is assumed to be the parent compound of the isomers under study. The band assignment of benzaldehyde[29] is as follows.

Table III.12 Benzaldehyde in (ethanol)

	K-band $\pi - \pi^*$	B-band (Benzenoid)	R-band $n - \pi^*$
λ_{max} (nm)	244	280	328
ϵ_{max}	15000	1500	20

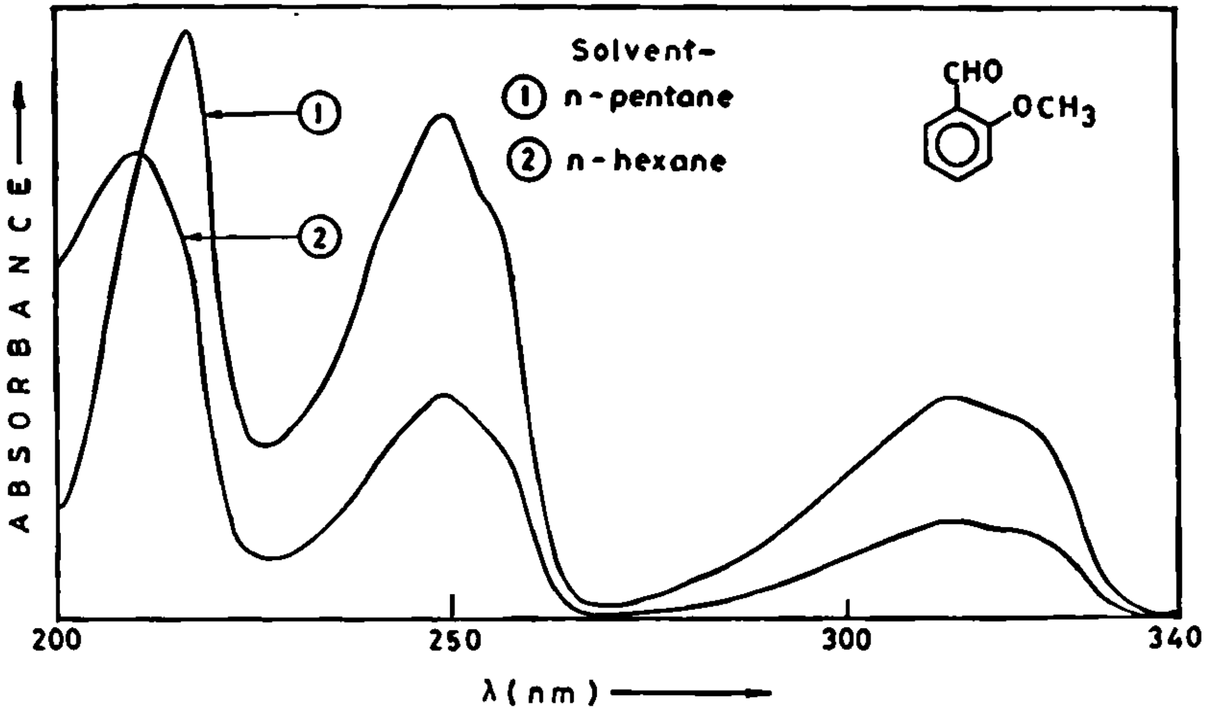


FIG.III.4 : ELECTRONIC ABSORPTION SPECTRA OF 2-METHOXYBENZALDEHYDE IN n-PENTANE, n-HEXANE.

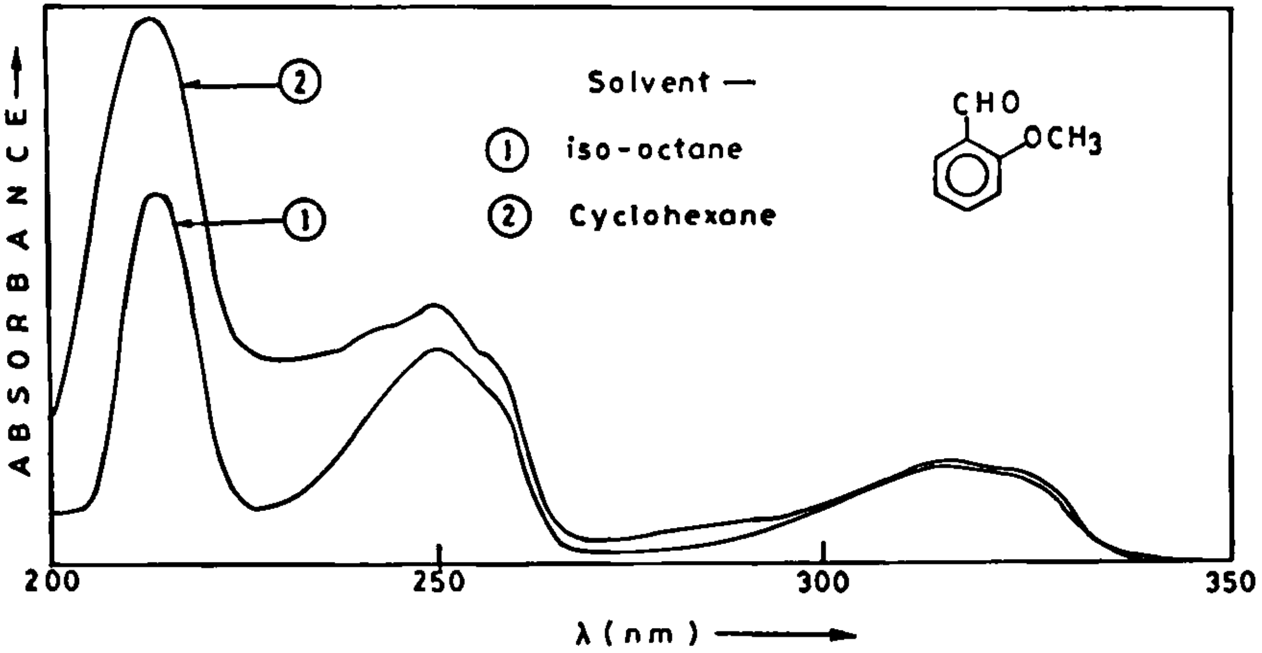


FIG.III.5 :ELECTRONIC ABSORPTION SPECTRA OF 2-METHOXYBENZALDEHYDE IN iso-OCTANE , CYCLOHEXANE .

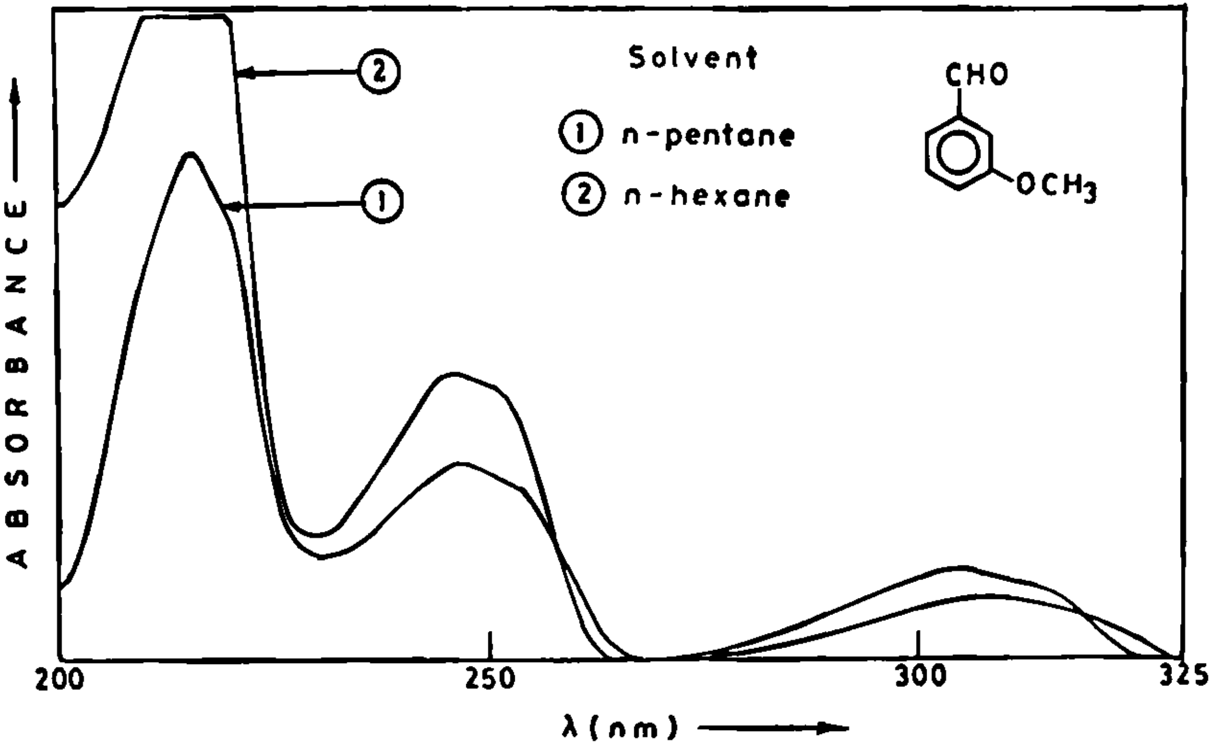


FIG.III.6 :ELECTRONIC ABSORPTION SPECTRA OF 3-METHOXY-BENZALDEHYDE IN n-PENTANE, n-HEXANE.

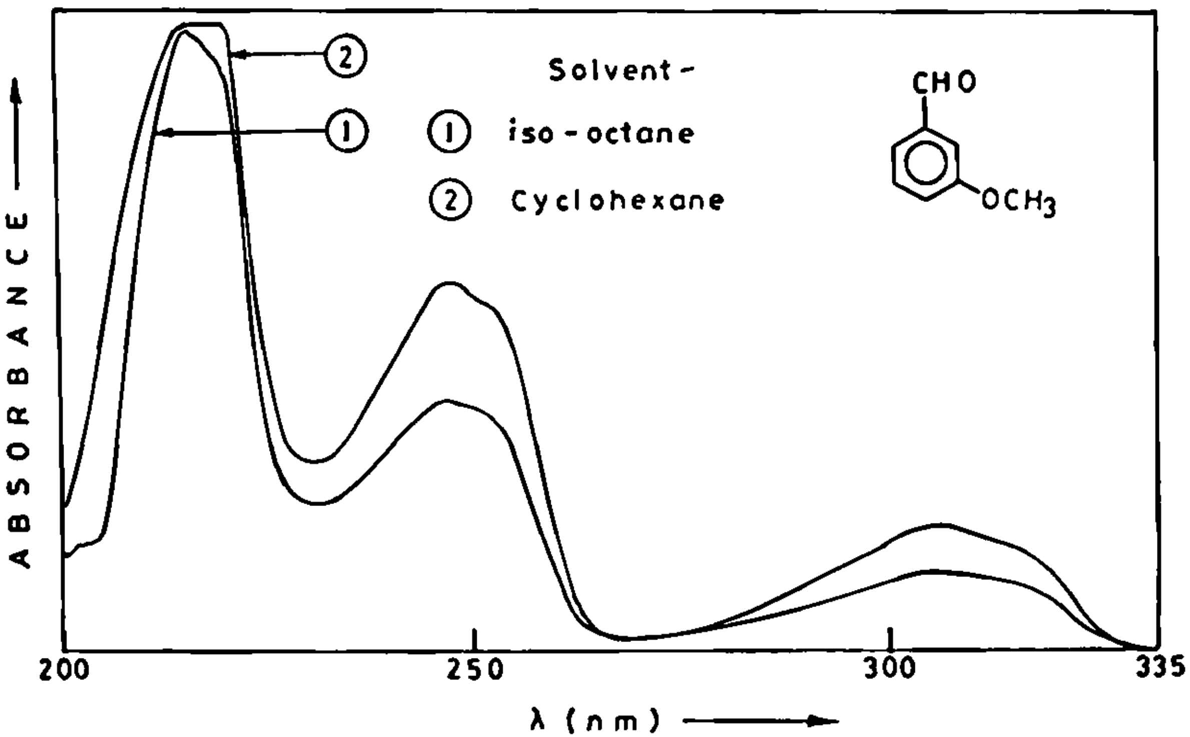


FIG.III.7 :ELECTRONIC ABSORPTION SPECTRA OF 3-METHOXY-BENZALDEHYDE IN iso-OCTANE, CYCLOHEXANE

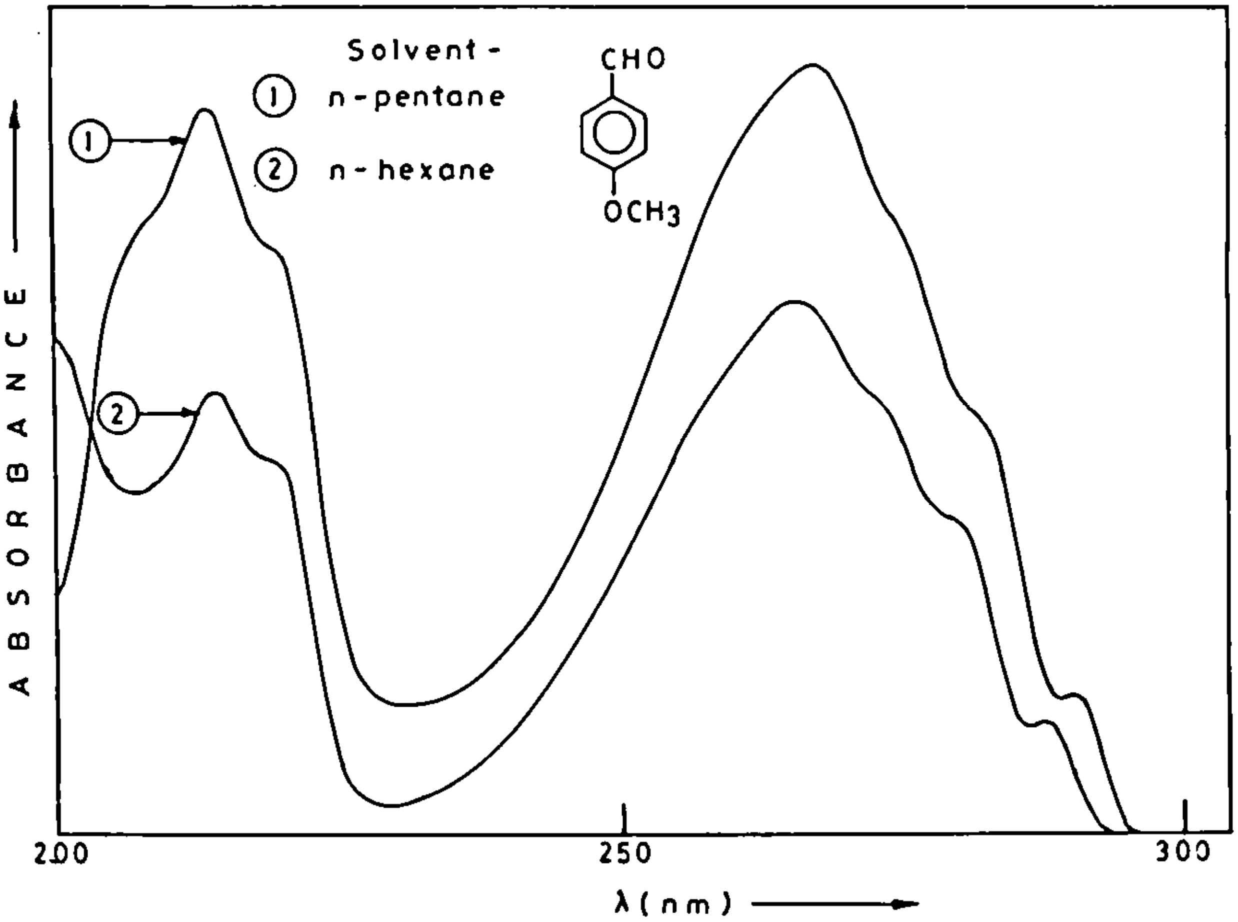


FIG.III.8 :ELECTRONIC ABSORPTION SPECTRA OF 4-METHOXY-BENZALDEHYDE IN n-PENTANE n-HEXANE.

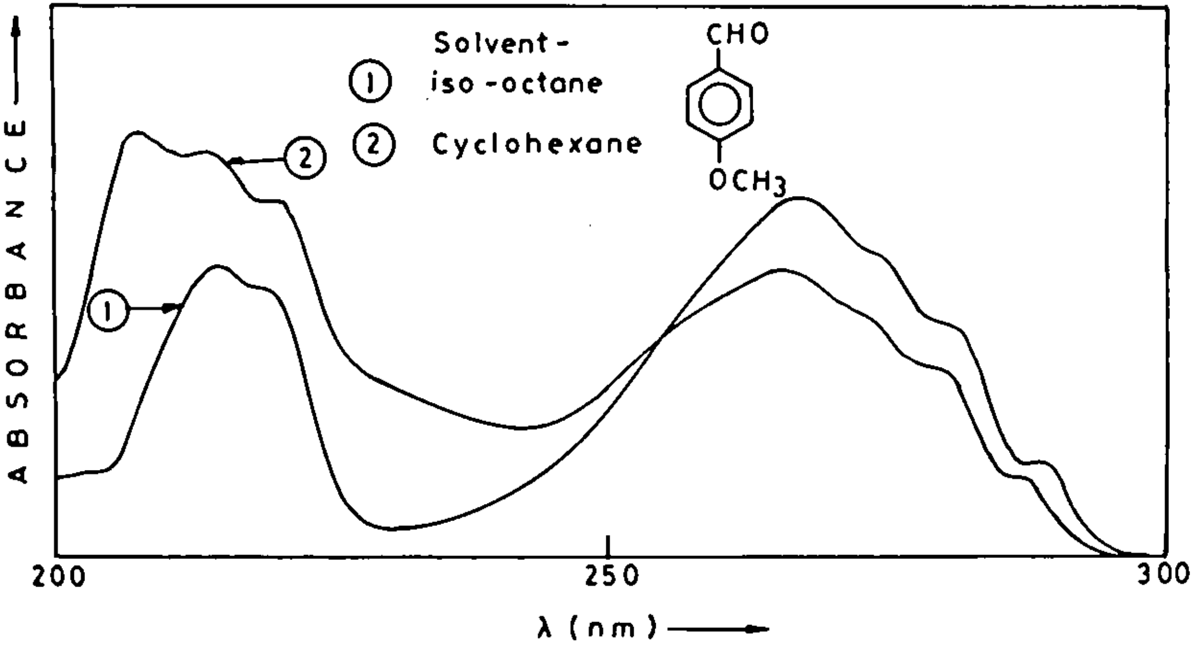


FIG.III.9 :ELECTRONIC ABSORPTION SPECTRA OF 4-METHOXYBENZALDEHYDE IN iso-OCTANE, CYCLOHEXANE.

The UV absorption spectra of benzaldehyde in hydrocarbon solvents were recorded in which the K-band ($\pi - \pi^*$) appears around 240 nm and B-band around 279 nm. It is well known that substitution on aromatic ring shifts the λ_{max} position. In the present case o- and m-OMe substitution shifts the band by + 7 nm each and in p-OMe, by + 25 nm. Thus the bands chosen for analysis are clearly the K-bands representing $\pi - \pi^*$ transition.

III.B.4 : Solvent effect on UV spectra and Dipole moments in Excited state

The solvatochromatic shifts of anisaldehydes have been measured in non-polar solvents like n-pentane, n-hexane, iso-octane and cyclohexane, in the present study. The dielectric constants and refractive indices of these solvents vary only marginally and hence the shifts observed are also very small. However distinct trends are exhibited in the shifts as follows :

(i) All the slopes of $\bar{\nu}_s$ and f(D), f(n) plots are negative i.e. as the dielectric constant or the refractive index of the solvent increases $\bar{\nu}_s$ value decreases.

(ii) The above variation are linear and smooth.

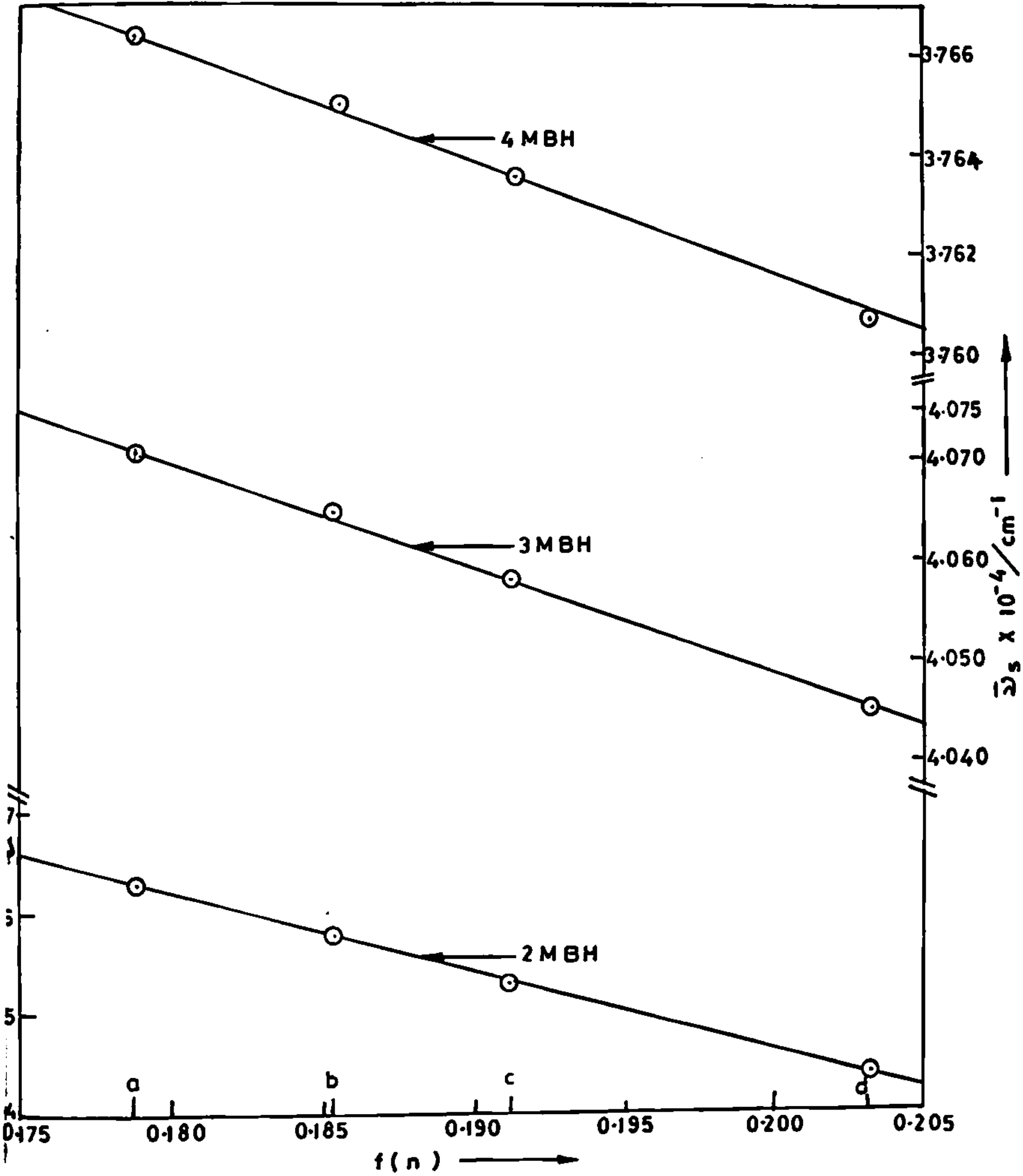


Fig.III.10: $\bar{\nu}_s$ vs f(n) plots for UV bands of MBH (Methoxy-benzaldehyde) 2,3,4
Solvents - a: n-pentane, b: n-hexane
c: iso-octane and d: cyclohexane

(iii) In the isomers the order of shift is m-anisaldehyde > o-anisaldehyde > p-anisaldehyde. These observations can be explained in the light of McRae equation as follows :

McRae[20] considers four contributing factors to the solvent effect.

(a) dispersion forces
(b) dipole-induced dipole forces
(c) dipole-dipole forces, and
(d) the quadratic Stark-effect caused between mutually induced dipoles of solutes and solvent molecules.

In the present system, since the solvents are non-polar, the contribution of factor (c) is negligible. Also, induction on solute due to dipolar field of solvent can be neglected. Thus factors (a) and (b) only are the major contributors to the shift.

The dispersion phenomenon is known to lower the potential of the system, hence the energy of the solvated levels is lowered, causing a red shifts as explained earlier (Chapter I). However, the magnitude of this factor does not change significantly for different solute solvent pairs. Thus the factor (b) is the deciding factor giving a particular slope to the graph. The higher f(n), f(D) values of the solvents indicate higher polarizability due to the solute dipole. Thus as the f(n) value increases, the solvation energy increases resulting in lowered $\bar{\nu}_s$ value.

Since the nature of interactions between solutes and the various solvents of this class is same, only the numerical value of interaction energy changes. This is reflected in linear variation of $\bar{\nu}_s$ with f(n) and f(D).

The lowering of $\bar{\nu}_s$ between cyclohexane and n-pentane for various solutes is recorded as red shift (non-polar) in the table given below.

Table III.13

Methoxy benzaldehyde isomer	μ_g (D)	$\bar{\nu}_s$ (non-polar) (cm^{-1})
o-anisaldehyde	4.37	188
m-anisaldehyde	2.96	259
p-anisaldehyde	4.09	56

To explain the trends observed in this table one should look into the nature of solute-solvent interactions. The polar solute induces Onsager's reaction field in the non-polar solvent. The interaction energy is given by the equation.[30]

$$U(r) = - \frac{1}{r^6} (\mu_2^2 \alpha_1)$$

where μ_2 is the inducing solute dipole moment, α_1 is the polarizability of the solvent and r is the effective distance between the two.

Upon excitation the μ_g value changes to μ_e and interaction energy changes to

$$U'(r) = - \frac{1}{r^6} (\mu_o^2 - \mu_g^2) \alpha_1$$

and between two solvents of polarizability α_1 and α_2

$$U''(r) = - \frac{1}{r^6} (\mu_e^2 - \mu_g^2)(\alpha_2 - \alpha_1)$$

Remembering that we are considering only the effect of induction and that the induction is in the direction opposite to that of the inducing moment, the $U''(r)$ will be observed as the superimposed effect over the red shift due to dispersive interaction. Naturally, if inducing moment is smaller, the original red shift will be least altered and with increasing dipole moment the red shift will be lowered. This has been observed in a series of trimethoxy benzaldehyde isomers[28] and in the present case also the redshift is lowered with increasing dipole moment of the solute.

However in p-anisaldehyde, the lowering is abnormally more. This is possible if the difference between μ_e and μ_g is inherantly smaller. This statement is obvious if one considers the simplified form of McRae equation.

$$\Delta\bar{\nu} = \left[(A + A') + B \right] \frac{n^2-1}{n^2+2}$$

where

$$B = (\mu_g^2 - \mu_e^2)\, hca_o^3$$

The explanation can be based upon 'particle in the box' theory. When an electron is delocalized over a longer conjugated circuit, the energy level separation $\mu_e - \mu_g$ will be smaller and vice versa. The delocalization in p-anisaldehyde is extended over longer distance, from methoxyl to formyl group as discussed previously and hence the difference $(\mu_e - \mu_g)$ is smaller in p-anisaldehyde. This is also evident from the following observation. The λ_{max} value of benzaldehyde in ethanol is red shifted in o- and m-anisaldehyde by only 7 nm while in p-anisaldehyde the shift is 25 nm.[7]

Thus these two effects together lower the red shift in p-anisaldehyde to the minimum level.

Thus the shift values and the trends observed thereof can be explained on the basis of solvation process and the McRae equation.

Table III.14 : Dipole moments in excited states and related properties of anisaldehydes as calculated by McRae using a_o by projection $(a_{o(p)})$ and a_o by molar refraction $(a_{o(R_D)})$.

Solute and μ_g/D	McRae a_o by projection					McRae a_o by molar refraction				
	Intercept $\bar{\nu}_v \times 10^{-4}$ / cm^{-1}	Slope $-B/cm^{-1}$	μ_e/D	$\Delta\mu_{e,g}$/D	$\mu_g + \Delta\mu_{e,g}$ / D	Intercept $\bar{\nu}_v \times 10^{-4}$ / cm^{-1}	Slope $-B/cm^{-1}$	μ_e/D	$\Delta\mu_{e,g}$/D	$\mu_g + \Delta\mu_{e,g}$ / D
o-anisaldehyde										
(4.37)	4.202	7768	5.57	0.95	5.32	4.20	7768	5.76	1.12	5.49
m-anisaldehyde										
(2.96)	4.262	10679	5.01	1.92	4.88	4.26	10679	5.26	2.23	5.19
p-anisaldehyde										
(4.09)	3.807	2300	4.46	0.27	4.36	3.80	2300	4.55	0.34	4.43

The Table III.14 lists the μ_e and $\Delta\mu_{e.g}$ values for the three isomers.

The experimental value $\mu_e = 5.2$ D for m-anisaldehyde is in fair agreement with the only reported value of $\mu_e = 6.2$ D.[4]

The largest value of $\Delta\mu_{e.g}$ in case of m-anisaldehyde is a natural consequence of localized electronic excitation. This can be compared with the extensively delocalized p-anisaldehyde case for which $\Delta\mu_{e.g}$ value is the smallest.

Thus we conclude that the excited state dipole moment values of anisaldehyde isomers, reported for the first time, can be explained with the above logic.

Also the method to estimate a_o by molar refraction methods appears to be practically simpler yet more logical. The μ_e values obtained with two different methods of evaluating a_o, do not differ significantly.

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SUMMARY

SUMMARY

Dipole moment values in benzene at 30 °C of o-, m- and p-anisaldehyde have been determined. The extrapolation method and the equation given by Halverstadt-Kumler and Deogadkar are used. Taking into account the factors affecting the stereochemistry, the most probable geometries of the anisaldehydes are predicted. Using the group moment values and the directions thereof, the theoretical dipole moments of these structures are evaluated. The close agreement of the structure and the experimental moment is supported by NMR shift conclusions. Hence with sufficient accuracy the molecular geometry of these molecules is predicted.

The effect of solvents on the electronic spectra of these molecules is studied. The shifts in λ_{max} values observed are interpreted. McRae equation and some modifications are used to evaluate the dipole moments of these molecules in the excited state. These values have been determined for the first time.