DIPOLE MOMENT OF THE CHARGE TRANSFER COMPLEX 1-ETHYL-4-METHOXY CARBONYL PYRIDINIUM IODIDE

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Dipole moment of a biologically important model compound: Charge transfer complex 1-ethyl-4-methoxy carbonyl pyridinium iodide was determined experimentally. A three component method was employed for this purpose, which is especially useful for determining the dipole moment of a salt insoluble in nonpolar solvents. The experimental dipole moment of this compound, hitherto unmeasured, was found to be $(37 \cdot 7 \pm 1 \cdot 0) \cdot 10^{-30}$ C m against the theoretical (contact) ion pair value of $46 \cdot 4 \cdot 10^{-30}$ C m.

Dipole moment (charge × distance) is a fundamental property of a molecule which gives information on the ionic character of bonds (in some cases of a particular bond) in a molecule, i.e. information on the polarity of a molecule[1-3]. It is a microscopic property[4] of molecules as compared to dielectric constant which is a macroscopic property.

Dipole moment measurements have been associated with the studies on the molecular structure i.e. its measurements can help in elucidating the structure or geometry of a molecule[5-6]. Generally IR spectra (rotational and vibrational), microwave spectra[7] and measurement of dielectric constant of a dilute solution of polar solute in nonpolar solvent gives the value of the dipole moment[5-6]. For simple molecules or conjugated hydrocarbons or simple heteroatomic molecules the dipole moment can be calculated theoretically[8]. In fact, instead of using variation method of minimizing energy for selecting good molecular orbital, an optimization of orbitals can be carried out which can give good or reasonable agreement of dipole moment with experiment[9].

Dipole moment of a polar molecule in a nonpolar solvent may be determined by a simple method based on application of the Clausius–Mosotti equation[5-6] or its modified form. The method involves the measurement of dielectric constant and refractive index of a series of dilute solutions of the polar compound.

Charge transfer complexes are an important and interesting class of polar compounds[10-13]. However, information regarding the dipole moments of charge transfer

complexes is almost lacking. Generally the measurement of dipole moment of a charge transfer complex by measuring the dielectric constant of its solution presents problem since one has to deal with a ternary system containing a donor (D), an acceptor (A), the charge transfer complex $(DA)_{CT}/(or D^+A^-)$ and the nonpolar solvent (S). The other alternative consists in considering the charge transfer complex as a contact ion pair and calculating the dipole moment from the van der Waals radii of the donor and acceptor[14].

Pyridinium iodides, which exhibit charge transfer property[4], can be isolated as pure crystalline solids. Pyridinium ion is biologically important as it forms a part of, say, NAD (refs[16-17]). The role of pyridinium ring *vis a vis* charge transfer complex formation had been proposed[16-17]. Synthesis and studies of the model compounds, pyridinium iodides, have provided information which has helped in the understanding of some biological reactions[16-17].

I
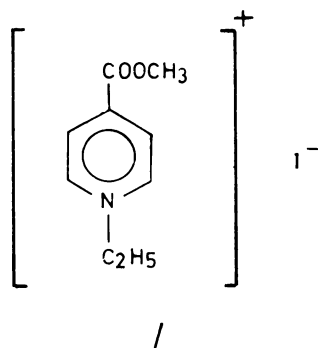
The model charge transfer compound, 1-ethyl-4-methoxy carbonyl iodide (*I*), has been extensively studied by Kosower and Mohammad[18-23]. The optical spectrum of *I* is solvent sensitive. The large solvent shifts observed for *I* in various solvents led Kosower to suggest it as a standard for the solvent polarity parameter — the Z-values[15]. The dipole moment of *I* has not been measured experimentally. However, a theoretical value of about $46.8 \cdot 10^{-30}$ C m has been estimated assuming it as a contact ion pair[14]. Therefore it is felt that an experimental value of the dipole moment of *I* may be helpful in understanding its structure and properties. In this report we present the results of our determination of the dipole moment of *I* in carbon tetrachloride, benzene and chloroform. Since 1-ethyl-4-methoxy carbonyl pyridinium iodide is not soluble in CCl_4 and C_6H_6, the dipole moment is measured in a three component system.

THEORETICAL

For a polar solute in a nonpolar solvent the Debye equation[24]

$$\mu^2 = \frac{9(P_\infty - P^a - P^e)\,kT}{4\pi N} \tag{1}$$

gives relationship between μ and the total polarization at infinite dilution (P_∞), the atomic and electronic polarizations $(P^a$ and $P^e)$. $(P_\infty - P^a - P^e)$ may be calculated from an equation[4] which avoids the need to measure the density of each solution

$$P_\infty - P^e - P^a = \frac{3M_2}{d_1}\,\frac{a_\varepsilon - a_n}{(\varepsilon_1 + 2)^2}\,, \tag{2}$$

where M_2 is the molecular weight of the solute, d_1 the density of the solvent, ε_1 the dielectric constant of the solvent, a_ε and a_n are the slopes of the linear relationship between weight fraction (w_2) and dielectric constant (ε_{12}) and the (square of the) refractive index (n_{12}) of the solution i.e.

$$\varepsilon_{12} = \varepsilon_1 + a_\varepsilon w_2\,, \tag{3}$$

$$n_{12}^2 = n_1^2 + a_n w_2\,. \tag{4}$$

Thus μ of a polar solute in a "nonpolar" solvent can be obtained from the following equation

$$\mu^2 = \frac{27kT}{4\pi N}\,\frac{M_2}{d_1(\varepsilon_1 + 2)^2}\,(a_\varepsilon - a_n)\,, \tag{5}$$

where N is Avogadro number, T is temperature and k is Boltzmann constant. Equation (5) may be used for determining the dipole moment of a polar solute in a binary mixture of solvents. In that case d_1 and ε_1 refer to the density and dielectric constant of the solvent mixture.

EXPERIMENTAL

Chemicals. 1-Ethyl-4-methoxy carbonyl pyridinium iodide was recrystallized from acetone[25]. Benzene was purified by shaking with H_2SO_4, then with water, dilute NaOH and water. It was dried first with $CaCl_2$ and then with 4A Linde molecular sieve and finally with CaH_2. Carbon tetrachloride was shaken with conc. H_2SO_4, washed with water, dried with $CaCl_2$ and then distilled from P_2O_5. Chloroform was washed with water, dried with $CaCl_2$, refluxed with P_2O_5 and distilled. All solvents were transferred into the measuring cell by passing through a 4A Linde molecular sieve column under nitrogen atmosphere. 1,2-Dinitrobenzene (BDH) was further purified by crystallizing from ethanol.

Instrumentation and measurement of dipole moment. The dipolemeter DMO1 (WTW) with DFL1 measuring cell was used for measuring dielectric constant. An Abbe refractometer was used for the measurement of refractive index. The temperature of the measuring cell and the refractometer was controlled to $\pm 0.2^\circ$C by a thermostat.

The usual method of determining dipole moment by measuring dielectric constants and refractive indices of dilute solutions of polar molecules in nonpolar solvents cannot be used for *I* since it is insoluble in CCl_4 and C_6H_6. Therefore the dipole moment of *I* was measured using a three-component system i.e. dilute solutions of *I* were prepared in $CHCl_3$–CCl_4 and $CHCl_3$–C_6H_6 mixtures of various compositions and their refractive indices and dielectric constants were measured. Application of Eq. (5) to three-component system was tested by determining the dipole moment of 1,2-dinitrobenzene (1,2-DNB) in $CHCl_3$–C_6H_6 and $CHCl_3$––CCl_4 mixtures as described below.

The dipole meter was calibrated using solvents (cyclohexane and benzene) of known dielectric constants. Then dielectric constant and refractive index of solutions of 1,2-DNB of various weight fractions in $CHCl_3$–CCl_4 or $CHCl_3$–C_6H_6 mixtures of varying compositions were measured. The slopes a_ε and a_n were obtained from ε and n^2 vs weight fraction plots. The dielectric constant (ε_1) and densities (d_1) of solvent mixtures were also measured. The dipole moment of 1,2-DNB was then evaluated for each solvent mixture using Eq. (5). Dipole moment of 1,2-DNB in "pure nonpolar solvent i.e. C_6H_6 or CCl_4" was determined by extrapolating measured dipole moment in solvent mixtures to zero $CHCl_3$ concentration. Similar procedure was adopted for the determination of dipole moment of *I* in $CHCl_3$–C_6H_6 and $CHCl_3$–CCl_4 mixtures.

RESULTS AND DISCUSSIONS

Results of the measurement of dipole moments of 1,2-DNB in $CHCl_3$–C_6H_6 mixtures together with slopes a_ε, a_n and dielectric constants (ε_1) and densities (d_1) of solvent mixtures are collected in Table I. Similar measurements were also performed in $CHCl_3$–CCl_4 mixtures. In Fig. 1 measured dipole moment of 1,2-DNB in mixed solvents is plotted against the concentration (in vol. %) of $CHCl_3$. The values of $21.0 . 10^{-30}$ C m and $21.6 . 10^{30}$ C m for the dipole moment of 1,2-DNB in "pure benzene" and "pure carbon tetrachloride" respectively correspond to zero concentration of $CHCl_3$. These values are obtained by least square regression analysis

TABLE I

Dielectric constants (ε_1), slopes and densities (d_1) of mixtures of $CHCl_3$–C_6H_6 and μ of 1,2––dinitrobenzene (observed in benzene $19.8 . 10^{-30}$ C m, from extrapolation $21.0 . 10^{-30}$ C m, reported $20.2 . 10^{-30}$ C m)

$c(CHCl_3)$ vol. %	ε_1	a_ε	a_n	d_1	$\mu . 10^{30}$ C m
15	2·71254	37·370	3·500	0·9116	21·40
20	2·81258	39·830	3·800	0·9263	21·51
25	2·82160	40·720	3·900	0 9420	21·68
30	2·91889	43·310	4·050	0·9587	21·70
35	3·00429	45·960	4·150	0·9742	21·88

of the experimental data and may be compared with the literature value[26] (20·2 .
. 10^{-30} C m) or the directly measured value of 19·8 . 10^{-30} C m in benzene. It is
seen that the agreement is reasonable i.e. about 5%. Therefore the method of deter-
mining the dipole moment of a polar compound in a three component system may
be adopted confidently for *I*.

Tables II and III summarize the results of the measurements of dipole moment
of *I* in solvent mixtures ($CHCl_3$–C_6H_6 and $CHCl_3$–CCl_4) of various compositions,
dielectric constants (ε_1) and densities (d_1) of mixed solvents and slopes a_ε and a_n.
The dipole moment of *I* in $CHCl_3$–CCl_4 is plotted against the concentration of
$CHCl_3$ in Fig. 2. The values of 38·6 . 10^{-30} C m and 36·6 . 10^{-30} C m are obtained

TABLE II

Dielectric constant (ε_1), slopes and densities (d_1) of $CHCl_3$–C_6H_6 mixtures and μ of PyI ($\mu =$
$= 36\cdot7 . 10^{-30}$ C m from extrapolation to $c(CHCl_3) = 0$) at 298 + 0·2 K

$c(CHCl_3)$ vol. %	$\varepsilon_1{}^a$	$a_\varepsilon{}^b$	$a_n{}^c$	$d_1{}^d$	$\mu . 10^{30e}$ C m
15	2·71254	63·530	5·850	0·9116	36·94
20	2·81258	67·233	6·200	0·9263	36·97
25	2·82160	68·900	6·350	0·9420	37·00
30	2·91889	73·760	6·920	0·9587	37·17
35	3·00479	77·433	7·330	0·9742	37·34

a Dielectric constant of pure solvent mixture; *b* slope of the plot of the dielectric constant of solu-
tions of various weight fractions of PyI vs weight fraction; *c* slope of the plot of refractive index
of solutions of various weight fraction, of PyI vs weight fraction; *d* density of pure solvent mix-
ture; *e* dipole moment of PyI in solvent mixture.

TABLE III

Dielectric constant (ε_1), slopes and densities (d_1) of mixtures of $CHCl_3$–CCl_4 and dipole moment
μ of PyI ($\mu = 38\cdot7 . 10^{-30}$ C m from extrapolation to $c(CHCl_3) = 0$) at 198 K

$c(CHCl_3)$ vol. %	ε_1	a_ε	a_n	d_1	$\mu . 10^{30}$ C m
15	2·66758	123·710	12·000	1·56320	39·4
20	2·67267	125·400	12·400	1·55659	39·9
25	2·67840	127·200	12·010	1·55024	40·2
30	2·68115	128·960	13·500	1·54405	40·4
35	2·68440	130·700	14·100	1·53816	40·7

for the dipole moment of I in "pure CCl_4" and "pure benzene" respectively from the least square treatment of the data. Thus an average value of dipole moment of I is $(37.7 \pm 1.01) \cdot 10^{-30}$ C m. However, a value of $43.4 \cdot 10^{-30}$ C m may be obtained for the dipole moment of I by extrapolation of the $CHCl_3$–CCl_4 data to 100% $CHCl_3$ concentration i.e. "pure $CHCl_3$". Interestingly the contact ion pair value[14] for the dipole moment of I calculated from the van der Waals radii of I^- and N in pyridinium ring is $46.4 \cdot 10^{-30}$ C m. Extrapolation of $CHCl_3$–C_6H_6 data gives a value of $39.4 \cdot 10^{-30}$ C m for the dipole moment of I in "pure $CHCl_3$". Thus the average value of μ for I in pure $CHCl_3$ would be $(41.4 \pm 2.0) \cdot 10^{-30}$ C m.

It may be noted that (i) the dipole moment of I is higher in CCl_4 than in C_6H_6 by $2.0 \cdot 10^{-30}$ C m (ii) dipole moment of I in CCl_4 or C_6H_6 differs from the theoretical value of $46.4 \cdot 10^{-30}$ C m calculated on the basis of ion-pair model (iii) extrapolation of measured μ in $CHCl_3$–CCl_4 and $CHCl_3$–C_6H_6 mixtures gives values of $43.4 \cdot 10^{-30}$ C m and $39.4 \cdot 10^{-30}$ C m respectively for the dipole moment of I in "pure $CHCl_3$" (iv) observed dipole moments vary with composition of the solvent mixture.

To explain points (i) and (ii) the following factors may be considered a) specific interaction of I with solvent b) the nature of bond in I (due to charge transfer complex and ion pair formation and c) mutual polarizability effect. The measured dipole moment of I in C_6H_6 is slightly less than the one in CCl_4 and it may be tempting to take this value $(\mu = 36.7 \cdot 10^{-30}$ C m as the true dipole moment of I. However this slight lowering of μ in C_6H_6 could be attributed to some extent to specific interaction of C_6H_6 with I (see, however, below) which reduces the dipole moment of I
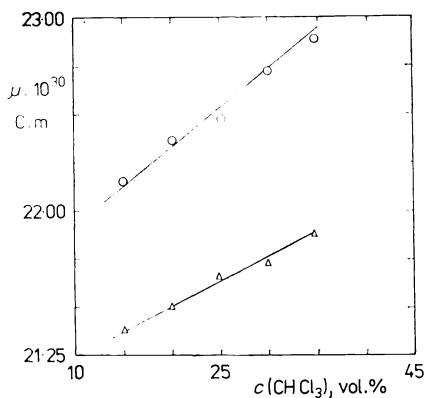

FIG. 1

Plot of measured dipole moment of 1,2-DNB vs concentration of $CHCl_3$ in $CHCl_3$–C_6H_6 ($\triangle$) and $CHCl_3$–CCl_4 ($\bigcirc$) mixture solvents
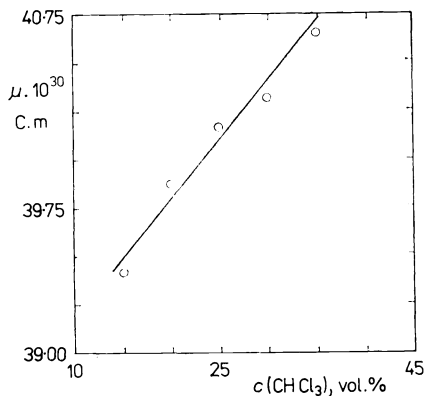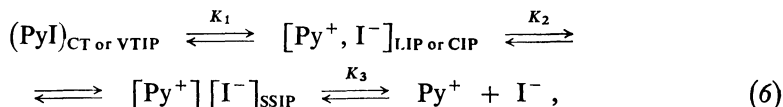
FIG. 2

Plot of measured dipole moment of 1-ethyl-4-methoxy carbonyl pyridinium iodide vs concentration of $CHCl_3$ in $CHCl_3$–CCl_4 mixture solvent

in this solvent. Alternatively some interaction between the two solvents, $CHCl_3$ and C_6H_6, (forming non-ideal solution) may be responsible in affecting the intercept and hence the value of μ.

It is worth considering the possibility of the interaction of I with $CHCl_3$, particularly at lower concentrations of $CHCl_3$ in mixed solvents. The extent of this particular interaction should be identical in $CHCl_3-C_6H_6$ and $CHCl_3-CCl_4$ solvent systems. The likely way in which I can interact specifically with $CHCl_3$ is through dipole–dipole interaction (orientation effect). The most favourable orientation of the two interacting dipoles corresponding to minimum energy is the one in which they are placed "head-to-tail". For this case the interaction energy is given by $E_{dipole-dipole} = -2\mu_A\mu_B/r^3$. For the interaction of I with $CHCl_3$, an estimate of $E_{dipole-dipole}$ may be made by taking $\mu(CHCl_3) = 3.34 . 10^{-30}$ C m, $\mu(I) = 37.7 .$ $. 10^{-30}$ C m, $r(CHCl_3) = 3.1 . 10^{-10}$ m, $r(I^-) = 3.0 . 10^{-10}$ m and $r = r(CHCl_3) +$ $r(I^-)$. Thus a value of 5.5 kJ is obtained for $E_{dipole-dipole}$ for the most favourable orientation. It is of the same order of magnitude as that arising from thermal agitation (2.5 kJ).

In summary it may be said safely that the specific interaction of I with C_6H_6, CCl_4 or $CHCl_3$ is not a significant factor in determining the dipole moment of I in these solvents. As regards to point (ii), the difference of $8.4 . 10^{-30}$ C m is of such an order of magnitude that it cannot be explained on the basis of mutual polarizability[27-28] or specific solute-solvent interaction as explained above.

There is no evidence, spectroscopic or otherwise, that either benzene or CCl_4 interacts significantly with I in any way other than influencing the charge transfer complex-ion pair structure equilibria[29] (Eq. (6)). It has been proposed that, depending upon the nature of the solvent, I exists in solution in the following equilibria[23].

$$(PyI)_{CT \text{ or } VTIP} \underset{}{\overset{K_1}{\rightleftarrows}} [Py^+, I^-]_{LIP \text{ or } CIP} \underset{}{\overset{K_2}{\rightleftarrows}}$$

$$\rightleftarrows [Py^+][I^-]_{SSIP} \underset{}{\overset{K_3}{\rightleftarrows}} Py^+ + I^- , \qquad (6)$$

where VTIP very tight ion-pair, CT charge transfer complex, LIP loose ion pair, CIP contact/caged ion pair and SSIP solvent separated ion-pair. The average value of $(37.7 \pm 1.0) . 10^{-30}$ C m in C_6H_6 and CCl_4 may be attributed to CT or VTIP structure of I, while the theoretical value of $46.4 . 10^{-30}$ C m reflects the value associated with LPI or CIP of I. These values of μ also reflect greater contribution of covalent bond in CT(VTIP) structure and of ionic bond in LIP(CIP) structure respectively. As regards to point (iii), the difference $4.04 . 10^{-30}$ C m in the extrapolated values of μ corresponding to "pure $CHCl_3$" may arise from a) specific interaction of I with benzene at low concentration of $CHCl_3$ and/or b) the non-validity of linear extrapolation to the limit of zero concentration of C_6H_6 in the case of $C_6H_6-CHCl_3$ system. As explained above contribution from a) may be slight while

factor b) may be valid. Unfortunately dipole moment measurement in pure $CHCl_3$ or with higher concentration of $CHCl_3$ in $CHCl_3$–C_6H_6 could not be carried out because of the limitation of the measuring cell used. However the value of $43\cdot7$. $.\ 10^{-30}$ C m is more acceptable in view the calculated value[14], $46\cdot4$. 10^{-30} C m, which is based on complete association of PyI in $CHCl_3$. The slight difference $3\cdot0$. $.\ 10^{-30}$ C m is within 10% of the theoretical value and this could arise from the existence of CT $\rightleftarrows$ LIP equilibrium in $CHCl_3$. Therefore dipole moment of I in this solvent may be expressed as

$$\mu_{obs} = X_{CT}\mu_{CT} + X_{IP}\mu_{IP} , \tag{7}$$

where X's are the mole fractions of the species in equilibrium. Thus K_1 in Eq. (6) can be calculated[23] from Eq. (8)

$$K_1 \frac{\mu_{CT} - \mu_{obs}}{\mu_{obs} - \mu_{IP}} . \tag{8}$$

Using $\mu_{CT} = 38\cdot7$. 10^{-30} C m, μ_{obs} (in $CHCl_3$) $= 43\cdot4$. 10^{-30} C m and $\mu_{IP} = 46\cdot4$. $.\ 10^{-30}$ C m, a value of $1\cdot55$ is obtained for K_1. It agrees reasonably with the value of $0\cdot5$ for K_1 (in $CHCl_3$) calculated from the proton NMR chemical shifts[23]. However using average values, $37\cdot7$. 10^{-30} C m for μ_{CT} and $41\cdot4$. 10^{-30} C m (in $CHCl_3$) for μ_{obs}, a value of $0\cdot54$ may be calculated for K_1. This later value of K_1 agrees well with the earlier reported value. Thus the value of μ for $(PyI)_{CT}$ may be taken as $(37\cdot7 \pm 1\cdot0)$. 10^{-30} C m while in $CHCl_3$ it may be taken as $(41\cdot4 \pm 2\cdot0)$. 10^{-30} C m. The variation in the dipole moment with the change in the composition of solvent mixture (point (iv) above) can be explained on the basis of equilibrium (Eq. (6)) and Eq. (7). Equilibrium constant K_1 for these solvent mixtures can be evaluated using Eq. (8).

In conclusion a value of $(37\cdot7 \pm 1\cdot0)$. 10^{-30} C m is obtained for the dipole moment of the charge transfer complex (or VTIP) of 1-ethyl-4-methoxy carbonyl pyridinium iodide using the method of three component system. The dipole moment of I in $CHCl_3$ is $42\cdot1$. 10^{-30} C m since it gives a reasonable value for K_1 when Eq. (8) is used.

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