CHAPTER II

EXPERIMENTAL
The samples of 1-bromo-2,4-, 1-bromo-2,5-, 1-bromo-3,4-, 1-bromo-3,5-difluorobenzenes and 3,4-, 3,5-difluoro-, 4-chloro-2-fluoro- anilines and 2,4-, 3,4-difluoroanisoles and 2-methoxy pyrazines used in this work were supplied by Aldrich Chemical Co., USA and were stated to be of very high purity. Out of these samples 3,5-difluoroaniline is a solid and all the other samples are liquids. All these samples were distilled (in the case of liquid compounds in vacuum) or recrystallised (in the case of solid compounds) using suitable solvents before use. Boiling and melting points and refractive indices were determined and comparing them with the literature values, the genuineness of the samples was confirmed.

INFRARED ABSORPTION

The infrared spectrophotometers used in the present investigation are (i) Perkin-Elmer Model 377 double beam automatic spectrophotometer with prism grating interchange in the region 200-4000 cm\(^{-1}\) and (ii) Hitachi Model 270-50 infrared spectrophotometer in the range 400-4000 cm\(^{-1}\). The infrared spectra were recorded in the pure liquid state in the case of liquid compounds and in nujol mull and in KBr pellets in the case of solid compounds. The peak frequencies were corrected with reference to the calibration spectrum of polystyrene film run under the same conditions.
In the case of solid compounds the wavenumbers of the infrared spectra taken in KBr pellets and in nujol mull agree in general up to \( \pm 10 \text{ cm}^{-1} \) in the case of most of the bands. The wavenumber data of both types of spectra as well as their reproductions are given elsewhere in the thesis. However, for purposes of discussing assignments, the wavenumber data of one type of spectrum only are used in the case of solid compounds.

**LASER RAMAN SPECTRA**

The laser Raman spectra of 3,4- and 3,5-difluoroanilines and 2-methoxypyrazine were recorded using a Cary Model Laser Raman spectrophotometer using \( \text{Kr}^+ \) laser with three Czerny-Littrow monochromators. The accuracy of measurements of the Raman line is a little better than \( \pm 5 \text{ cm}^{-1} \).

**ULTRAVIOLET ABSORPTION**

Figure 2.1 gives the schematic representation of the experimental set-up used for obtaining the ultraviolet absorption spectra. The continuous radiation coming from the source is made parallel by the double convex lens \( L_1 \). This parallel beam of radiation passes through the vapour under investigation held in a absorption tube \( T \) and is condensed by a second lens \( L_2 \) onto the slit of the spectrograph \( M \) which photographs the absorption spectrum.
FIG 2.1 UV absorption set-up
Carl Zeiss high pressure xenon arc is employed as a source of continuous radiation. The absorption tubes of path lengths 5, 10, 25 cms are all of quartz and provided with fused quartz windows of diameter 2.5 cms. The absorption tubes are provided with a side tube B as shown in Figure 2.2 which serves as the container for the compound under investigation. C is the side tube of quartz joined to D with a quartz to pyrex graded seal. For path lengths more than 25 cms and in between 10 and 25 cms a modified absorption tube is used. The main part of the absorption tube is made of pyrex and is connected on either side to fused quartz windows, through graded seal. Absorption tubes of different path lengths are obtained by varying the length of the main pyrex tube.

The substance (previously vacuum distilled) to be investigated is transferred to the container B and by keeping the container in a cooling mixture of ice and salt, the complete absorption tube is evacuated for nearly four hours and then the constriction A made near the container is sealed off.

The absorption tube is then introduced into the path of radiation for studying the absorption spectrum. The absorption spectrum is studied at different vapour pressures by keeping the container tube at different temperatures. For temperatures below the room temperature the absorption tube is held in position by retort
FIG. 2.2 Absorption Tube
stand and the container tube is immersed in a Dewar flask having ice-salt mixture, ice-acetone mixture or ice-cold water. The study of the absorption spectra at these low temperatures is helpful in fixing the 0,0 band of the system.

For temperatures higher than the room temperature it is necessary to maintain the main portion of the absorption tube at a slightly higher temperature (about 10°C) than the container in order to prevent condensation of vapour on the windows. The uniform heating of the cells is done by winding thermal tapes in the case of shorter cells. For the longer ones the cells are wrapped with asbestos papers and a nichrome wire is wound over this maintaining a distance 8 mm between two consecutive turns. To account for the heat loss due to radiation near the ends of the cell, the number of turns per cm is increased at these places. The current through the nichrome wire is regulated by a variac and with this arrangement temperature upto 200°C could be attained throughout the length of the cell.

In the present study of the ultraviolet absorption spectra of 1-bromo2,4-, 1-bromo-2,5-, 1-bromo-3,4- and 1-bromo-3,5-difluorobenzenes, absorption path lengths varying from 3 cms to 50 cms were used and the temperature of the absorption cell was varied from 0° to 100°C. In the case of 3,4-, 3,5-difluoro- and 4-chloro-2-fluoroanilines and
2,4-, 3,4-difluoroanisoles, the absorption path lengths were varied from 25 cms to 100 cms and the temperature of the absorption cell was varied from room temperature to 150°C, while in the case of 2-methoxy pyrazine the absorption path lengths varying from 5 cms to 50 cms were used, and the temperature of the absorption cell was varied from 0°C to 75°C.

For photographing the ultraviolet absorption spectra, Hilger Littrow spectrograph was employed. Kodak analysis plates were used to record the spectra and the exposure time in general was varied from 10 minutes to 2 hours.

Measurements were made with a Hilger comparator reading to 0.001 cm. Iron arc comparison spectra were also taken for every absorption spectrum and wavelengths were calculated in short steps using Hartmann dispersion formula each step covering about 50 Å. Measurements were made on various plates, taken under different conditions (at different temperatures and different pathlengths) each plate being measured at least three times. The mean values of different measurements were taken for the wavelength of each band. The wavelengths of the bands were converted into wave numbers in vacuum using table of wavenumbers [1]. The accuracy of the measurements varies from 5 to 10 cm\(^{-1}\), the former for sharper bands.
and the latter for diffused bands. The intensities are visual estimates and vary with the temperature and pathlength used. As regards the intensities of the bands (infrared, Raman and Ultraviolet) the following general notation is employed to indicate them.

vs = very strong; vsb = very strong and broad
s = strong; sb = strong and broad
ms = medium strong; msb = medium strong and broad
m = medium, wb = weak and broad
w = weak, vwb = very weak and broad
vw = very weak; sh = shoulder.

The ultraviolet absorption spectra of 1-bromo-2,4-, 1-bromo-2,5-, 1-bromo-3,4- and 1-bromo-3,5- difluorobenzenes, 3,4-, 3,5- difluoro and 4-chloro-2-fluoro-anilines, 2,4- and 3,4- difluoroanisoles were also recorded on a Hitachi U-3200 UV/VIS spectrophotometer in the vapour phase using a pathlength of 5 cm at room temperature in the range $\lambda 2000-2500 \, \text{Å}$.

Further the ultraviolet absorption spectra of all the compounds except methoxypyrazine mentioned earlier, in different solvents (spectroscopic grade purity), were also recorded on a Hitachi 150-20 and Hitachi U-3200 UV/VIS spectrophotometers using cells of thickness 1 cm in the range $\lambda 2500 \, \text{Å}$ to $\lambda 3500 \, \text{Å}$. 
DETERMINATION OF GROUND STATE DIPOLE MOMENT

The electric dipole moment of a polar molecule at a radio frequency can conveniently be determined by carrying out measurements of static dielectric constants of their dilute solutions of graded concentration in a non-polar solvent. The dielectric constant of the dilute solution medium is usually measured as the ratio of capacitance with the dielectric and air as the media in a suitable fabricated cell of usually small capacitance. Since the solutions are dilute, the dielectric constants so measured are not expected to differ much from solution to solution. Thus, an accurate determination of small changes of capacitance is essential. In the present work these small capacitances were measured with the help of a single transistor-based crystal controlled oscillator. The necessary dielectric sample holder consisted of two concentric brass cylinders kept in position with small glass strips (to achieve electric isolation) and their leads were coated with gold. This assembly was kept in a glass tube with a ground glass stopper and the capacitance of the empty cell (air) was found to be about 25 pF.
EXPERIMENTAL SET-UP

The set-up is essentially a crystal controlled oscillator utilising a resonance method as shown in Figure 2.3, the quartz crystal was connected between the collector and the base whereas the tank circuit was connected to the collector of the RF-transistor. The latter is designed for 1 MHz ($L_1 C_1$) with a variable condenser of 250 pF ($C_2$) along with the dielectric cell of small capacitance between its plates ($C_x$) which could be connected across $C_x$. The precision variable condenser ($C_2$) used here was supplied by Muirhead, England and a small change in the capacitance up to 0.05 pF could be accurately measured.

OPERATION

When a power of d.c. 5 V is given to the collector circuit, the quartz crystal gets power and begins to oscillate, initiating oscillatory current in the base of the transistor. This, in turn energizes the tuned circuit in the collector. By turning the variable condenser $C_2$ the oscillations will be stabilised to 1 MHz at a particular setting of the condenser. This is indicated by a detector (frequency counter) across emitter lead. Whenever the empty cell is connected across $C_x$ the oscillator ceases to oscillate. By turning $C_x$ again, to a next setting stable oscillations begin at
Circuit Diagram

Q. Quartz crystal
R₁ 50 K
R₂ 10 K
R₃ 560
Cₓ Cell
C₂ Murrhead variable air condenser 250 pf
C₁ 250 pf
L₁ Inductance

FIG. 2.3
1 MHz. Thus the change in the condenser setting indicates the capacitance added to the tuned circuit. Thus the change in the capacitance from concentration to concentration of dilute solutions in the dielectric cell can be noted.

MEASUREMENTS

Measurements were made as indicated below:

Precision condenser reading without cell = \( C_1 \)
Precision condenser reading with empty cell = \( C_2 \)
Precision condenser reading with sample in the cell = \( C_3 \)

The dielectric constant (\( \varepsilon \)) was determined by the ratio of change in capacitance with and without the sample.

\[
\varepsilon = \frac{C_1 - C_3}{C_1 - C_2}
\]

Since the leads connecting the cells to the tank circuit of the oscillator would have some capacitance, for an accurate determination of dielectric constant, the capacitance of these connecting leads must also be included. If \( C_x \) represents this capacitance the dielectric constant of the medium would be
The value of $C_x$ was determined by carrying out measurements on several standard liquids, both polar and non-polar from their known values of $\varepsilon$.

For the determination of dipole moment, two more parameters, namely, the refractive index of the solution and the density of the solvent are required besides the dielectric constant. The refractive index for sodium "D" line of various dilute solutions and solvents were determined using the Abbe' type refractometer whereas the density was measured using a specific gravity bottle.

EVALUATION OF DIPOLE MOMENT

For the determination of the dipole moment, the modified method due to Guggenheim was followed [2]. According to this method, the dipole moment is given by the relation,

$$\mu = 0.0128 \sqrt{P_0 T} \text{ Debye units.}$$

where $P_0 = \frac{3}{(\varepsilon + 2)^2} \times \frac{M_2}{d_1} \times \Delta$ is the orientation polarisation.
of the solute and

\[ \Delta = \Delta' - \Delta'' = \left( \frac{e_{12} - e_1}{W_2} \right) - \left( \frac{n_{12}^2 - n_1^2}{W_2} \right) \]

is the difference between the intercepts of the plots \((e_{12} - e_1/W_2)\) versus \(W_2\) and \((n_{12}^2 - n_1^2/W_2)\) versus \(W_2\) extrapolated to infinite dilution. The quantities \(n, d, M, W\) and \(T\) are the refractive index, density, molecular weight, weight fraction and absolute temperature respectively. The suffixes 1, 2 and 12 refer to the relevant quantities of solvent, solute and solution, respectively.
REFERENCES
