CHAPTER II
Experimental Technique
2.1. General

The experimental arrangements for obtaining the ultraviolet absorption spectra of the aromatic organic compounds in different states and in solutions and for studying the infrared and the Raman spectra and the state of polarization of the Raman lines are described in the following sections.

2.2. Samples and their purification

The samples chosen for the present investigation were obtained from different reputed manufacturers like E. Merck, B.D.H. (England), Schuchardt (Germany), Fluka etc. Some of the samples were of chemically pure grade and were used without further purification. A few samples were subjected to fractional and vacuum distillation before being used. The solvents (isobutyl alcohol, ethyl alcohol, cyclohexane, n-hexane, carbon tetrachloride, chloroform, nujol mull etc.) used in the study of ultraviolet and infrared absorption in solution were purified and dried by standard methods and they were tested by observing their absorbances in the spectral region under consideration.
A. Ultraviolet absorption spectra

2.3. Source and the spectrograph

A hydrogen discharge tube of pyrex glass about 50-cm long and provided with a plane quartz window at one end was used as a source of ultraviolet radiation. Purified hydrogen gas, drifted over fused calcium chloride was circulated at a suitable low pressure through the discharge tube so that a steady discharge without any striation was maintained. The discharge tube was run by a 2.0 KV, 2.0 KW transformer. An Adam Hilger El quartz spectrograph (E 478) having dispersion of about 2.5 A/mm in the 2600 A region was used to photograph the absorption spectra. Spectrograms were taken on Kodak spectrum Analysis Film No.1. The film mounted on the plate holder was backed by a metal sheet to avoid local kinks in it. Iron arc spectrum was photographed with a Hartmann diaphragm on each film for comparison.

2.4. Arrangements for the photographing the absorption spectra

The schematic arrangements for photographing the absorption spectra of the aromatic organic compounds are shown in Figure 2.1. For studying the absorption spectra of
**SCHEMATIC DIAGRAM OF THE EXPERIMENTAL ARRANGEMENT**

E - ELECTRODES; D - DISCHARGE TUBE; W - QUARTZ WINDOW; B - BRASS FRAME;
C - ABSORPTION CELL; L₁ - L₂ - FUSED SILICA LENSES; O - LIQUID OXYGEN;
V - FUSED QUARTZ DEWAR; S - SLIT OF THE SPECTROGRAPH.
the compounds in the vapour phase, the purified sample in the form of liquid or solid was introduced in a small glass bulb reservoir attached to the centre of the vapour absorption cell. The absorption cells were cylindrical glass tubes of different lengths whose ends were closed by two plane parallel plates of fused quartz with "Araldite" fixer followed by curing at a temperature of 180°C for eight hours. After the compound (liquid or solid) was introduced in the reservoir bulb the absorption tube was evacuated so that the tube was filled with the vapour of the compound at the saturation pressure corresponding to the temperature of the reservoir. The vapour pressure corresponding to any desired low temperature was obtained by simply immersing the bulb in a suitable coolant while the absorption tube was left at the room temperature. For increasing the vapour pressure the absorption tube was kept inside a cylindrical electrical heater while the reservoir bulb was placed inside a box-type electrical heater. The heaters could be maintained at any desired temperatures. The temperature of the absorption tube was always kept about 5°C to 10°C higher than that of the bulb to ensure avoidance of condensation of liquid on the windows. To bring out the vibrational structure of the spectrum as clearly as possible, absorption tubes of
different path lengths kept at different temperatures were used. Continuous ultraviolet radiation from the hydrogen discharge tube, made slowly convergent by a pair of quartz lenses placed in front of the absorption tube was allowed to pass through the vapour as far axially as possible and the beam coming out of the exit window was made incident on the slit of the spectrograph. Time of exposure required to photograph the spectra varied from 5 minutes to 45 minutes, the slit width being about 0.05 to 0.1 mm depending on the width of the absorption bands.

For recording the ultraviolet absorption bands of the compounds in the liquid state at room temperature and in the solid state at 77°K or 93°K very thin films of thickness usually of the order of a few microns were required. Such thin uniform films of desired thickness were obtained by trial. The absorption film thus formed between the two quartz plates was held in an aluminium frame and the cell was introduced in the ultraviolet ray path to photograph the spectrum. For studying the absorption spectra at low temperatures the absorption cell described above was provided with copper fins attached to the bottom of the aluminium frame and the whole arrangement was placed inside a Dewar vessel made of fused quartz so
that the copper plates are kept well immersed in liquid oxygen (or nitrogen) contained in the Dewar vessel. Liquid oxygen (or nitrogen) level in the Dewar vessel was maintained just below the lower edge of the quartz plates. The rapid current of cold oxygen (or nitrogen) vapour coming out of the Dewar vessel due to evaporation of liquid oxygen (or nitrogen) prevented any moisture from entering into the Dewar vessel even up to a small distance below the vessel's open end.

Purified solvents, as stated earlier, were used to obtain the absorption spectra of the compounds in dilute solutions of the order of $10^{-3}$ to $10^{-4}$ M. Generally the solution absorption spectra at room temperature were taken with all quartz sintered absorption cells of path lengths varying from 5 to 15 minutes. For obtaining low temperature rigid glass spectra, the absorption cells were made of hollow cylindrical brass (or copper) tubes of different lengths, varied from .1 cm to 1 cm, the ends of which were closed by two plane parallel plates of fused quartz with "Araldite" fixer. These cells were held in the aluminium frame and the low temperature rigid glass spectra were taken in the same manner as the low temperature thin film spectra as stated in the earlier paragraph. The exposure
time for the rigid glass spectra varied from 20 minutes to 1 hour. In all cases the slit width was about 0.1 mm.

The extinction co-efficients ($\varepsilon$-value) of some of the compounds in dilute solutions in pure solvents were measured with an all metal spectrophotometer (Spectromom-201, Budapest, Hungary) and Beckman DU2 ultraviolet spectrophotometer.

2.5. Determination of wave lengths

The microphotometric records of the spectra were taken with a Kipp and Zonen Moll microphotometer. In order to find out the wave lengths of the absorption peaks accurately from the microphotometric records, a suitable iron arc line was chosen in each spectrogram and a corresponding linear scratch mark was made with a sharp pin across the absorption spectrum to serve as a reference line. A microphotometric record of the iron arc spectrum was then taken from the same film with the same magnification ratio (1.6 : 1) as used for the absorption spectrum. The wave lengths corresponding to the peaks of the ultraviolet absorption bands in the records were determined by measuring the distance of the peaks from the reference
line and finding out the wave lengths at the same distances from the corresponding reference line in the record due to the iron arc spectrum photographed on the same spectrogram. The wave lengths of the sharp bands could be measured with an accuracy of about ± 10 cm⁻¹. For broader bands the uncertainty in measurement could be higher.

B. Infrared absorption spectra

2.6. Arrangement for recording infrared spectra of compounds in the liquid state and in solutions

The infrared spectra of compounds were recorded with a Perkin-Elmer Model 21 infrared double beam spectrophotometer fitted with rock salt optics and wave number scale in the counter. The slit was adjusted by putting the resolution dial at 927. Atmospheric absorption had to be correctly compensated by adjusting the balance in order to get reliable results. The amplifier gain of 6.0 was found most satisfactory for operation. The calibration was checked by recording the atmospheric water vapour band at 3740 cm⁻¹ with single beam arrangement and also by recording the standard absorption bands of polystyrene film. The whole instrument was kept in an air conditioned room having 40% relative humidity at 26°C. The absorption
spectra due to pure samples were investigated either by forming thin capillary films between a pair of rock-salt discs or by using very thin cells. In recording infrared absorption spectra of compounds in dilute solutions in different solvents, cells of different thickness were used. Matched compensation cells with respective solvents were placed in the path of the reference beam to eliminate the absorption due to solvents.

C. Raman spectra and the state of polarization of the Raman lines

2.7. Arrangement for studying the Raman spectra

The Raman spectra of the compounds in the liquid state at room temperature (26°C - 36°C) were studied with an arrangement shown in Figure 2.2. The source of light L, sent its radiations in the direction shown by the arrow, into the transparent tube of pyrex glass containing the experimental liquid through the cylindrical lens L. One end of the transparent tube had an optically flat window W, and the other end was drawn into a "horn shaped" form, H as indicated in the figure. The horn H, and a portion of the tube near the window were painted black to trap steady
SCHEMATIC DIAGRAM OF THE EXPERIMENTAL ARRANGEMENT FOR STUDYING THE RAMAN SPECTRA
reflected radiations. Radiation scattered along the direction \( R \) (perpendicular to \( I \)) was focussed on the slit of the spectrograph by a lens. The spectrograph used in the present investigation was a "Fuess glass" spectrograph having a dispersion of about 13 A/mm and 19 A/mm in the Hg 4047 A and 4358 A regions respectively. The group of Hg lines 4047 A and 4358 A were employed for exciting the spectra. In some case dilute solution of sodium nitrate was used in the path of the incident radiation as a filter to eliminate continuous background. The Raman spectra were photographed on Ilford Zenith plates. Iron arc spectrum was superimposed on each spectrogram for comparison.

The arrangement for studying the character of polarization of the Raman lines of a compound in the liquid state at room temperature was almost the same as those described above, with some modifications. In this case a refracting double image prism was placed between the window of the Raman tube and the slit of the spectrograph and the two components of the scattered light were simultaneously focussed on the slit of the spectrograph one above the other and photographed.