Chapter 3

EXPERIMENTAL

3.1 Introduction:

The experimental technique used in the research work are incorporated in brief in the following sections. Melting points were determined in open capillary tubes and are uncorrected. Formation of the compounds was routinely checked by TLC on silica gel-G plates of 0.5 mm thickness and spots were located by iodine and UV. Compounds were purified by using column chromatography.

3.2 Materials:

The following chemicals were obtained from Sisco Research Laboratories Pvt. Ltd:-

I. 2,4-Dinitrophenyl Hydrazine extra pure AR ,Assay — min. 99%
II. Acetophenone extra pure Assay (GC) — min.99%
III. o-Dichlorobenzene pure C6H4CI2 Assay (GC) — min 99%
IV. Para Bromo acetophenone Min Assay (GC 98%)
V. Para Chloro Acetophenone, Min Assay (GC 98%),
VI. Para methoxy acetophenone Min Assay (GC 99%)
VII. p-Dimethylamino- Benzaldehyde extrapure AR; Assay — min.99%
VIII. Silica Gel 230-400 mesh
IX. Silica Gel 60-120 mesh
X. Silica Gel G for TLC (with binder)
XI. Sodium Hydroxide Pellets 97% purified NaOH Assay — min.97%
XII. α-Naphthol pure Assay (GC) — min.98%
XIII. β-Naphthol extrapure AR; Assay(GC) — min.99%

The following chemicals were obtained from Spectrochem Pvt. Ltd., Mumbai:-

I. 4-Acetylpyridine >98%
II. 4-Chlorobenzaldehyde > 98%
III. 4-Hydroxybenzaldehyde >99%

IV. 9-anthraldehyde >97%
V. Hydrochloric acid
VI. Anisaldehyde
VII. Benzaldehyde ACS, Iso
VIII. Benzaldehyde Min Assay (GC 98%)
IX. Dimethyl Sulphate > 98%
X. Hydrazine Hydrate 99%
XI. N,N-Dimethylformamide > 99%
XII. O-Chlorobenzaldehyde >98%
XIII. Para hydroxy benzaldehyde Min Assay (GC 98%)
XIV. Phosphorous Oxychloride > 99%
XV. Pyridine-4-Aldehyde > 98%
XVI. Triethylene Glycol >99%

2-Naphthaldehyde, Triphenyl Amine was purchased from Alfa Aesar.
Chemical reagents were used without further purification

3.3 General techniques:

3.3.1 Single Crystal X-Ray Diffraction:

The single crystal XRD data of was collected on a graphite monochromatic MoKa X-ray source of wavelength 0.71073 Å. Here the crystal-to-detector distance was fixed at 4 cm with a detector area of 6×6 sq cm. The structure was solved by direct methods using Bruker SHELXTL Software Package.

3.3.2 Fourier Transform Infrared (FTIR) Spectral Analysis:

The FTIR spectral analyses were carried out to identify the chemical bonding and molecular structure of the material. The FTIR spectra were recorded by using Shimadzu- FT-IR Spectrometer, Perkin Elmer Spectrum Version 10.4.00 in the wave number range 400– 4000 cm^{-1}.

3.3.3 UV-Visible and Fluorescence Spectroscopy:

Steady-state absorption spectra were recorded on a Shimadzu UV-1601PC absorption spectrophotometer.

Fluorescence spectra were obtained with a PerkinElmer LS 45 spectrofluorometer and all the spectra were corrected for the instrument response function

3.3.4 NMR:

^{1}H (400 MHz, 800 MHz spectrometer) and ^{13}C (125 MHz) using Nuclear magnetic resonance spectra were recorded on Bruker 400 Ultrashield, Bruker 800 Ultrashield Plus tetramethylsilane as internal standard. The chemical shift values are expressed in δ (ppm) units while J values in Hz.

3.3.5 z-scan experimental technique

The z-scan technique is a sensitive measurement technique based on self-focusing effect. It is an accepted technique for characterizing third order nonlinear optical materials. Through this technique, simultaneous measurement of nonlinear index of refraction n_2, and nonlinear absorption coefficient β, which are related to the real and imaginary parts of third order nonlinear optical susceptibility $\chi(3)$, respectively can be estimated. So, it is helpful when both nonlinear absorption and nonlinear refraction is behind the optical nonlinearity in a material. Generally, in this technique, a gaussian laser beam is focused using a lens on the sample and by translating the sample through the focus, the change in the far-field intensity pattern is examined. The sample is moved along the axis of the laser beam, taken to be the z-axis, from the left to the right of the focal point. To get the closed aperture z-scan data, transmitted intensity is measured by placing an aperture in front of the detector. The amount of light getting through this aperture is measured as a function of the sample position. To obtain the open aperture z-scan data, the transmittance is measured without aperture when the sample is moved along the z-direction. The material under investigation itself behaves as a thin lens for the laser beam propagating through it. The effective focal length of the material changes depending on the intensity of the converging laser beam, the change in intensity distribution in the far-field zone is measured by the closed aperture z-scan technique. The medium also has nonlinear absorption, which is significant in the open aperture measurement. Thus, collectively, the closed aperture and the open aperture data allow calculating values of both n_2 and β.

3.3.6 z-scan experimental details:

The schematic experimental setup for z-scan is shown in Figure. 3.1. Basically, in this technique a gaussian laser beam is focused, using a lens (L) of 20 cm focal length. The experiments were performed using a linearly polarized Q-switched, frequency doubled Nd:YAG laser (home made in RRCAT, Indore) which produces 38 ns at 1064, SHG was used with 28 ns pulses at 532 nm, at a pulse repetition rate of 1 Hz. The resulting beam waist radius at the focus was 58 micron (ω_0). d is the diameter of the aperture, found to be 1 mm, the transmission was 0.1. The corresponding Rayleigh length was found to be 4 mm**.** For solution z-scan measurements, cuvette of 1 mm thickness was used. The sample (S) was moved along the laser beam axis using a computer controlled (PC) translation stage. The detector (D) was placed at a distance of about 100 cm from the focal spot, i.e., Z = 0. A circular aperture (I) of diameter 5 mm was placed in front of the detector and the detector output was monitored as the sample was translated along the laser beam axis from Z= –150 mm to Z= +150 mm. Input intensity ranged from (50 – 700) µJ. The second harmonic of the laser beam was used for the measurements; the laser power was reduced to several degree by using a variable neutral density filter. Gentec ED 200 Energy Meter was also used.

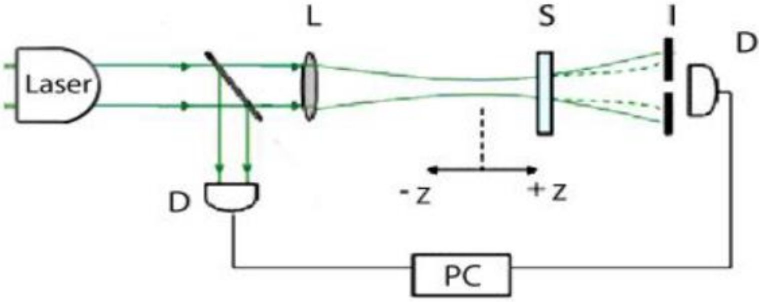

Figure 3.1: Schematic diagram of z-scan setup.

3.3.7 Up-Conversion photoluminescence spectra collection:

The excitation source was a Ti:Sapphire laser (Tsunami BB, Spectra Physics, 179-1098nm, ~70 fs, 82 MHz. The laser energy can be tuned from 1.459 eV to 1.653 eV. The spectral width of the laser at full width at half maximum (FWHM) was nearly 28 meV). In order to select a narrow bandwidth of emission wavelengths an H20Vis Jobin Yvon monochromator was placed at the entrance of a PMC-100-4 photomultiplyer tube (Becker and Hickl GmbH).

3.4 Conclusion:

The synthesized compounds were characterized and their optical properties were also investigated using the mentioned techniques.