CHAPTER FOUR

Estimation of the First Hyperpolarizability of a Series of p-Nitroaniline Derivatives

4.1 Introduction

The electro-optic effect can be brought about in a polymer matrix by the addition of non-centrosymmetric dipolar molecules. These molecules possess high second order susceptibilities and are sometimes called nonlinear optical chromophores.\(^1\) The molecular second order susceptibility is also termed as the first hyperpolarizability \(\beta_{ijk}\), where \(i, j\) and \(k\) refers to molecular axes. The synthesis and study of molecules with large first order hyperpolarizabilities is important due to the potential applications of such molecules in nonlinear optics. Many components for optical signal processing and communication devices can be made out of materials possessing high electrooptic coefficients.\(^2\)

This chapter gives the details of the molecules studied for nonlinear optical properties. The molecular parameters including ground state dipole moment, excited state dipole moment and the first hyperpolarizability were estimated. The aim was to make a selection of molecules with comparatively higher values for the figure of merit explained in Section 1.5.3.

The estimation of the first hyperpolarizability was done using the two level microscopic model of \(\beta_{ijk}\). The techniques available to measure this
important parameter are second harmonic generation,\textsuperscript{3} electric field induced second harmonic generation (EFISH)\textsuperscript{4} and hyper-Raleigh scattering.\textsuperscript{5} An estimation of first hyperpolarizability can be done using the simplified two level model also.\textsuperscript{6} This method requires the excited state dipole moment, which can be estimated using solvatochromism and the ground state dipole moment which can be estimated using the Debye-Guggenheim method. Solvatochromism involves studying the effect of solvent polarity on the molecule’s absorption and fluorescence spectra.

4.2 Molecules studied

All molecules were synthesized in our lab and the details are given elsewhere.\textsuperscript{7,8} The structure of the molecules studied are given in Fig. 4.1, 4.2 and 4.3. The main difference between the molecules was in the number of alkyl spacers connecting the acceptor group and the donor group.

![Fig. 4.1: N,N-bis(4-bromobutyl)-4-nitrobenzenamine (1a).](image1)

![Fig. 4.2: N,N-bis(4-[(n-aminoalkyl)amino]butyl)-4-nitrobenzenamine.](image2)

Molecules with this general structure were labeled as 2a, 2b, 2c, 2d and 2e.
Molecules studied

Figure 4.3: N, N-bis(4-[n-(ethyl amino)alkyl amino]butyl)-4-nitrobenzenamine. Molecules with this general structure were labeled as 3a, 3b, 3c and 3d.

The number of alkyl units was varied from n = 2 to 6, correspondingly there were a total of 10 molecules under study. In the second set, n = 5 was not available for studies. Table 4.1 shows the labeling of the molecules adopted during the experiments.

<table>
<thead>
<tr>
<th>n</th>
<th>IUPAC Name</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>N,N-bis(4-bromobutyl)-4-nitrobenzenamine</td>
<td>1a</td>
</tr>
<tr>
<td>2</td>
<td>N,N-bis(4-[(2-aminoethyl)amino]butyl)-4-nitrobenzenamine</td>
<td>2a</td>
</tr>
<tr>
<td>3</td>
<td>N,N-bis(4-[(3-aminopropyl)amino]butyl)-4-nitrobenzenamine</td>
<td>2b</td>
</tr>
<tr>
<td>4</td>
<td>N,N-bis(4-[(4-aminobutyl)amino]butyl)-4-nitrobenzenamine</td>
<td>2c</td>
</tr>
<tr>
<td>5</td>
<td>N,N-bis(4-[(5-aminopentyl)amino]butyl)-4-nitrobenzenamine</td>
<td>2d</td>
</tr>
<tr>
<td>6</td>
<td>N,N-bis(4-[(6-aminohexyl)amino]butyl)-4-nitrobenzenamine</td>
<td>2e</td>
</tr>
<tr>
<td>2</td>
<td>N,N-bis(4-[2-(ethylamino)ethylamino]butyl)-4-nitrobenzenamine</td>
<td>3a</td>
</tr>
<tr>
<td>3</td>
<td>N,N-bis(4-[3-(ethylamino)propylamino]butyl)-4-nitrobenzenamine</td>
<td>3b</td>
</tr>
<tr>
<td>4</td>
<td>N,N-bis(4-[4-(ethylamino)butylamino]butyl)-4-nitrobenzenamine</td>
<td>3c</td>
</tr>
<tr>
<td>6</td>
<td>N,N-bis(4-[6-(ethylamino)hexylamino]butyl)-4-nitrobenzenamine</td>
<td>3d</td>
</tr>
</tbody>
</table>
4.3 Determination of ground state dipole moment ($\mu_g$)

The figure of merit of nonlinear optical chromophores is highly dependent on the ground state dipole moment and the first hyperpolarizability of the molecule.\(^9\) The refractive index modulation achievable in a photorefractive guest host system depends on the figure of merit\(^10\) and in turn on the dipole moment of the material. As described in Section 1.5, the tendency of the molecules to align antiparallel is determined by the ground state dipole moment. Thus an idea about the magnitude of this molecular property is useful when deciding the poling requirements to induce non-centrosymmetry. The ground state dipole moment can be determined by the Debye Guggenheim method, where the actual measurement is the static dielectric constant of a series of solutions of varying weight fraction of the molecule in a non-polar solvent. The value is then extrapolated to infinite dilution to calculate the dipole moment using equation 4.1.\(^11\)

\[
\mu_g^2 = \frac{3\varepsilon_0 kT}{N_A} \frac{9}{(\varepsilon_0 + 2)(n_0^2 + 2) \rho_0} \frac{M}{\rho} \left( \frac{\partial \varepsilon}{\partial \omega} \right)_0 \quad (4.1)
\]

Here M is the molar mass of the molecule, $\omega$ is the weight fraction, $\varepsilon_0$, $n_0$ and $\rho_0$ are the dielectric constant, refractive index and the density of pure solvent respectively. $N_A$ is the Avogadro number and $\varepsilon_0$ is the permittivity of vacuum. The term $(\partial \varepsilon/\partial \omega)_0$ represents the variation of dielectric constant with weight fraction at infinite dilution.

The above equation assumes that the refractive index of a solution of the molecule has negligible dependence on its weight fraction.\(^11\) The refractive index of the solutions were measured using an Atago DRM2 refractometer and the variation with weight fraction was found to be negligibly small, so that the equation can be safely applied. To calculate dielectric constants, several concentrations of the molecules under investigation were prepared in toluene (being a non-polar solvent) and filled between the plates of a parallel plate capacitor with variable plate separation and the capacitance was measured as a function of plate separation.
(d) using an HP 4277A LCZ meter operating at 10 KHz. Capacitance of the capacitor was measured in this manner first filling it with the solution under test and later with spectroscopic grade toluene. If $C_s$ is the capacitance with the solution and $C_t$ is the capacitance with toluene, the dielectric constant of the solution can be determined from the ratio of the slopes of the plots of $C$ vs $1/d$. The dielectric constant of the solution, $\varepsilon_s$, was determined using equation 4.2.

$$\varepsilon_s = \varepsilon_t \frac{K_s}{K_t}$$  \hspace{1cm} (4.2)

Here $\varepsilon_t$ is the dielectric constant of toluene, $K_s$ is the slope of the plot of $C_s$ with $1/d$ and $K_t$ is the slope of the plot of $C_t$ with $1/d$.

Toluene ($\varepsilon_r = 2.379$) was used for the standardization of the measurement. The parameter $\partial\varepsilon/\partial\omega$ was extracted from the plot of dielectric constant with weight fraction of the molecule. Plots of the variation of dielectric constant with weight fraction of the solute are shown in Fig. 4.4, 4.5, 4.6, 4.7 and 4.8. Equation 4.1 was used to calculate the ground state dipole moment of the molecule.

![Figure 4.4: Variation of the dielectric constant with weight fraction of 1a and 2a.](image)
Determination of ground state dipole moment ($\mu_g$)

Figure 4.5: Variation of the dielectric constant with weight fraction of 2b and 2c.

Figure 4.6: Variation of the dielectric constant with weight fraction of 2d and 2e.

The range of weight fractions of the second set of molecules was less than the previous set. As the method assumes the values at infinite dilution, this change in concentration will not affect a comparison of the results.\textsuperscript{11}
Determination of ground state dipole moment ($\mu_g$)

Figure 4.7: Variation of the dielectric constant with weight fraction of 3a and 3b.

Figure 4.8: Variation of the dielectric constant with weight fraction of 3c and 3d.

The results obtained are given in Table 4.2. A unit conversion can be achieved by noting that 1 Debye = $3.33564 \times 10^{-30}$ C.m = $10^{-18}$ esu.
Table 4.2: Ground state dipole moments of the molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\mu_g$ (D)</th>
<th>Molecule</th>
<th>$\mu_g$ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>9.78</td>
<td>2e</td>
<td>12.63</td>
</tr>
<tr>
<td>2a</td>
<td>8.88</td>
<td>3a</td>
<td>4.43</td>
</tr>
<tr>
<td>2b</td>
<td>8.48</td>
<td>3b</td>
<td>11.75</td>
</tr>
<tr>
<td>2c</td>
<td>10.20</td>
<td>3c</td>
<td>16.85</td>
</tr>
<tr>
<td>2d</td>
<td>8.06</td>
<td>3d</td>
<td>7.47</td>
</tr>
</tbody>
</table>

4.4 Determination of excited state dipole moment ($\mu_e$)

The excited state dipole moment is another quantity which shows the extent of charge transfer after excitation by radiation of sufficient energy. If the difference between the ground and excited state dipole moments is very large, the charge transfer is also very large provided the bond length remains unaltered upon excitation. The determination of excited state dipole moment is very important and there are many methods proposed in the literature. Gas-phase stark effect is one of such methods which involve examination of the splitting of rotational lines due to externally applied electric field.\(^\text{12}\) A simple method is to analyze the solvent polarity dependence of the absorption and emission maxima (solvatochromism) of the molecule under consideration to extract $\mu_e$.\(^\text{9}\)

4.4.1 The solvatochromic effect

Solvatochromism is the change in the position, intensity, and shape of absorption or emission bands of a molecule due to the change in polarity of the solvent.\(^\text{13}\) The spectral shift is caused by the electric field experienced by a molecule embedded in such a solvent. This electric field, called reaction field, arises from the polarization of the surrounding solvent molecules due
Solvatochromic measurements

to the dipole moment of the solute.\textsuperscript{12}

The solvatochromic method was used for the estimation of the first hyperpolarizability of the molecules. Although the accuracy of the method was less compared to more accurate methods like second harmonic generation or hyper Raleigh scattering, the purpose was to screen the synthesized chromophores. For this purpose the experiment was well suited.

4.4.2 Solvatochromic measurements

The solvatochromic estimation of $\mu_e$ involves no laser measurements. The absorption and fluorescence spectra in solvents of varying polarity were needed for the analysis. In order to get a gradual variation of the polarity of the solvents, a binary solvent mixture comprising the polar solvent acetonitrile and the non-polar solvent toluene were used for the solvatochromic analysis.\textsuperscript{8} A polar molecule has unequal sharing of electrons between the atoms constituting it.

The refractive index and the dielectric constant of the mixture at various proportions were measured to compute the bulk solvent polarity parameter $F(\varepsilon, n)$ defined\textsuperscript{14} by equation 4.3.

\begin{equation}
F(\varepsilon, n) = \left\{ \frac{2n^2 + 1}{n^2 + 2} \{ (\varepsilon - 1)(\varepsilon + 2) - (n^2 - 1)(n^2 + 2) \} \right\}, \tag{4.3}
\end{equation}

Here $n$ and $\varepsilon$ are the refractive index and the dielectric constant of the mixture respectively. There are mainly two methods proposed in the literature for the analysis of the solvatochromic data.

4.4.2.1 Method 1

In this method, the emission $\nu_f \text{ cm}^{-1}$ and absorption $\nu_a \text{ cm}^{-1}$ bands are analyzed based on the following equations.\textsuperscript{15}

\begin{equation}
\nu_a - \nu_f = m_1 F(\varepsilon, n) + \text{Constant}, \tag{4.4}
\end{equation}

\begin{equation}
\nu_a + \nu_f = -m_2 \{ F(\varepsilon, n) + 2g(n) \} + \text{Constant}, \tag{4.5}
\end{equation}

Here $g(n)$ is another parameter given by $g(n) = (3/2)(n^4 - 1)/(n^2 + 2)^2$. Equations 4.4 and 4.5 show that the plots of $\nu_a - \nu_f$ and $\nu_a + \nu_f$ with $F(\varepsilon, n)$
and \([F(\varepsilon, n) + 2g(n)]\) would be linear with slopes \(m_1\) and \(m_2\) respectively. These slopes are further given by,

\[
m_1 = \frac{2(\mu_e - \mu_g)^2}{\hbar c a^3},
\]

\[
m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{\hbar c a^3},
\]

where \(h\) is the Planck’s constant and \(c\) is the velocity of light. \(a\) is the Onsager cavity radius which can be calculated using the density \((d)\) and the molecular weight \((M)\) of the molecule using the relation \(a^3 = (3M/4\pi dN_A)\).\(^{16}\)

Values of \(m_1\) and \(m_2\) can be obtained from the plots of \(\nu_a - \nu_f\) and \(\nu_a + \nu_f\) with \(F(\varepsilon, n)\) and \([F(\varepsilon, n) + 2g(n)]\).

Even small errors in the estimated value of the cavity radius can lead to very large errors as the value enters as cubed in the above equations. Taking the ratio \(m_2/m_1\) enables the determination of the excited state dipole moment without using the value of \(a\). The excited state dipole moment of the molecule can be expressed in terms of the known value of the ground state dipole moment as \(\mu_e = \mu_g(1 + x)/(x - 1)\), where \(x = m_2/m_1\).

### 4.4.2.2 Method 2

In the second method, the analysis is based on the dimensionless solvent polarity parameter \(E_T^N\) proposed by Reichardt,\(^{13}\) which is given by equation 4.8.

\[
E_T^N = \frac{E_T(solvent) - 30.7}{32.4},
\]

where \(E_T(solvent) = 28591/\lambda_{max}(\text{nm})\), and \(\lambda_{max}\) corresponds to the peak wavelength in the red region of the intramolecular charge transfer absorption of the molecule 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridino) phenolate.\(^{13}\) This molecule, also called Reichardt’s dye, shows a large solvatochromic effect. The absorption maxima of the dye in solvent mixtures of varying polarity were experimentally determined and used for the calculation of \(E_T^N\). This reduced the error due to the presence of impurities in the
mixture as each solvent mixture was separately analyzed for its polarity value before use.

The plots of $E_N^T$ and $F(\varepsilon, n)$ versus the weight fraction of Acetonitrile in the mixture is shown in Fig. 4.9. The plots were nonlinear when the percentage of toluene was higher, thus for the analysis of the data, only solvent mixtures showing a linear variation of the polarity parameters were used. Detailed physical properties of the toluene-acetonitrile mixture is available in the literature.$^{17}$

![Graph showing variation of $E_N^T$ and $F(\varepsilon, n)$ with weight fraction of Acetonitrile](image)

Figure 4.9: Variation of the polarity parameters with weight fraction of Acetonitrile

For the determination of the excited state dipole moment $\mu_e$, the Stoke’s shift $\nu_a - \nu_f$ was calculated from the absorption and fluorescence spectra. Here $\nu_a$ and $\nu_f$ denote the absorption and fluorescence band maxima respectively, in $cm^{-1}$. The Stoke’s shift ($\nu_a - \nu_f$) was analyzed as a function of the polarity of the solvent. Variation of ($\nu_a - \nu_f$) with $E_N^T$ was linear with more than 98 % correlation to a linear fit. The variation of the Stoke’s shift with $E_N^T$ is shown in Fig. 4.10 for the molecules 1a, 2a, 2b, 2c, 2d and 2e. For the other set of molecules the variation is given in Fig. 4.11.
Figure 4.10: Graphs showing the linear variation of Stoke’s shift with $E_T^N$ for 1a, 2a, 2b, 2c, 2d and 2e.

Figure 4.11: Graphs showing the linear variation of Stoke’s shift with $E_T^N$ for 3a, 3b, 3c and 3d.

The Stoke’s shift is related to the difference in dipole moments and the Onsager radii of the molecule and the dye by equation 4.9.

$$v_a - v_f = 11307.6 \left( \frac{\Delta \mu^2 a_D^3}{\Delta \mu_D^2 a^3} \right) E_T^N + \text{Constant} \quad (4.9)$$

Here $\Delta \mu = \mu_e - \mu_g$ is the difference between the ground and excited state dipole moments of the molecule being studied and $\Delta \mu_D$ is that of Reichardt’s dye. In the expression, the Onsager radii of both the dye ($a_D$) and the molecule ($a$) enters as a ratio and thus the error due to the uncertainty in the value of $a$ is minimized. As the values of $a_D$ and $\Delta \mu_D$
were known (6.2Å and 9D respectively\textsuperscript{13}), the excited state dipole moment of the material under study could be evaluated from the plot of $\nu_a - \nu_f$ with $E_N^T$. Results of the calculation are given in Table 4.3.

Table 4.3: Excited state dipole moments of the molecules estimated from the solvatochromic analysis.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\mu_e$ (D)</th>
<th>Molecule</th>
<th>$\mu_e$ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>14.96</td>
<td>2e</td>
<td>19.07</td>
</tr>
<tr>
<td>2a</td>
<td>14.53</td>
<td>3a</td>
<td>9.50</td>
</tr>
<tr>
<td>2b</td>
<td>14.55</td>
<td>3b</td>
<td>17.58</td>
</tr>
<tr>
<td>2c</td>
<td>15.88</td>
<td>3c</td>
<td>22.56</td>
</tr>
<tr>
<td>2d</td>
<td>24.12</td>
<td>3d</td>
<td>14.67</td>
</tr>
</tbody>
</table>

4.5 Estimation of the first hyperpolarizability ($\beta$)

Based on the solvatochromic measurements described above, one can estimate the first hyperpolarizability of the molecule with the two level microscopic model of $\beta$\textsuperscript{6,18}. In this model, the contributions from all excited states other than the first excited state are neglected\textsuperscript{6}. The following equation gives the value of $\beta$ in terms of experimentally measurable quantities.

$$\beta = \frac{3\omega_{eg}^2(\mu_e - \mu_g)\mu_{eg}^2}{2\hbar^4(\omega_{eg}^2 - 4\omega^2)(\omega_{eg}^2 - \omega^2)} \quad (4.10)$$

where $\omega_{eg} = 2\pi c/\lambda_{max}$ and $\mu_{eg}$ = the transition moment, calculated from the area under the absorption band\textsuperscript{6}. The area was determined by doubling the area of half of the absorption band if the spectrum was not symmetric about the peak frequency\textsuperscript{11}.

The solvatochromic method gives only one dominant component of the tensor quantity $\beta_{ijk}$. It is assumed that the molecules have the donor and acceptor groups located such that the charge transfer takes place primar-
illy along the axis of the permanent ground state dipole moment of the molecule.\(^6\) Thus Eq. 4.10 gives \(\beta_{xxx}\) (or \(\beta_{CT}\)) (charge transfer).

Photorefractive materials can be used for beam amplification in the two beam coupling geometry. Chromophores for such photorefractive guest host systems must not be absorbing at the operating wavelength to get an effective two beam coupling gain.\(^{19}\) The molecules described here have only low absorption in the visible region of the spectrum. All molecules showed an increase in dipole moment on excitation by light. This showed that there was a higher degree of charge transfer taking place. The results are given in Table 4.4.

Table 4.4: Compilation of the results obtained on the different molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(\beta) ((10^{-30})) esu</th>
<th>(9\mu_g\beta(10^{-46})) esu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>387</td>
<td>3.77</td>
<td>3.32</td>
</tr>
<tr>
<td>2a</td>
<td>393</td>
<td>3.22</td>
<td>2.57</td>
</tr>
<tr>
<td>2b</td>
<td>395</td>
<td>2.84</td>
<td>2.17</td>
</tr>
<tr>
<td>2c</td>
<td>397</td>
<td>2.64</td>
<td>2.42</td>
</tr>
<tr>
<td>2d</td>
<td>398</td>
<td>5.16</td>
<td>3.74</td>
</tr>
<tr>
<td>2e</td>
<td>399</td>
<td>4.07</td>
<td>4.63</td>
</tr>
<tr>
<td>3a</td>
<td>400</td>
<td>2.87</td>
<td>1.14</td>
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<td>3b</td>
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<td>4.20</td>
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<tr>
<td>3c</td>
<td>401</td>
<td>2.77</td>
<td>4.20</td>
</tr>
<tr>
<td>3d</td>
<td>402</td>
<td>5.56</td>
<td>3.74</td>
</tr>
</tbody>
</table>

4.6 Summary and conclusions

The purpose of the work outlined was to evaluate the nonlinear optical properties of the synthesized molecules so as to select those possessing high values of photorefractive figure of merit. The ground and excited state dipole moments were determined which gave insight into the possibility of
light induced charge transfer in these molecules. It could be seen that, on
excitation by light, the charge redistribution was such that it resulted in
a higher value for the dipole moment. The estimate of the ground state
dipole moment gave the relative tendency of the investigated molecules to
align antiparallel in pairs in the bulk so that a net second order nonlinear
optical effect could be absent. This molecular parameter was kept in mind
when deciding the requirement of poling for the photorefractive samples.

The solvatochromic method assumes that the molecule is spherical and
this method is suitable to small molecules. The estimation of $(\beta_{ijk})$
suffers from errors associated with the Onsager radius and the size of the molecule
though some of them can be circumvented by appropriate processing of
the data. Measures were taken to reduce the errors by using solvents
of maximum purity and they were characterized as described in Section
4.4.2.2, each time before use. As the aim was to screen the molecules to
find the ones with maximum value for $(\beta_{ijk})$, errors can be neglected even
if it is as high as 20%.

It is reported that the length of the alkyl spacer connecting the donor to
the acceptor moiety has major effect on the value of $(\beta_{ijk})$. This approach
of increasing the value of $\beta$ has the advantage that the absorption maxima
of the molecule is not getting changed as there is no change in the effective
conjugation length of the material. The main aim of the present work
was to study the possibility of the synthesized molecules for application
to photorefractive polymers as the absorption of these molecules do not
fall well in to the visible region. This was stimulated by the fact that for
highly efficient photorefractive applications, the molecule for electro-optic
functionality should not absorb at the operating wavelength. There was
only small change in the absorption peak of the these materials, as shown
in Table 4.4, but a steady increase in hyperpolarizability was not achieved.
A small increase in the figure of merit was observed.

The chromophores with odd number of alkyl spacers showed higher
$(\beta_{ijk})$ values. It is reported that the lower values for even number of alkyl
units can be due to a centrosymmetric arrangement of the molecules. A deep investigation of this interesting effect was not attempted. The
molecules with high values for the product $\mu\beta$ were selected for the preparation of photorefractive guest host systems. The experimental techniques for the evaluation of the electro-optic coefficients are described in Chapter 5 along with the results obtained.

References


References


