According to electron donor-electron acceptor concept, structure property relationships of push-pull NLO-phores based on the theoretical and experimental work have led to the definition of molecular engineering rules. These definitions indicate that the hyperpolarizability ($\beta$), characterizing the molecular second order NLO efficiency, depends on the strength of the donor and acceptor groups, on the extent of the $\pi$-conjugated path and, for conjugating spacers based on aromatic systems, on the resonance stabilization energy of the aromatic system.\(^1\) Intensive studies regarding the NLO efficiencies of molecules containing $\pi$-conjugated spacers are seen in the literature.\(^2\) But the effect of alkyl spacers has not been studied properly.

This chapter is divided in to two parts; in the first part, quantum chemical calculations on the linear and nonlinear electric polarizabilities of dipolar molecules separated by alkyl spacers have been performed on $\mathrm{O}_2\mathrm{N}-\mathrm{Ph}-\mathrm{N}=\mathrm{N}-\mathrm{Ph}(\mathrm{CH}_2)_n-\mathrm{Ph}-\mathrm{N}=\mathrm{N}-\mathrm{Ph}-\mathrm{NO}_2$, $n = 1-12$. These molecules exhibit a very strong odd-even behavior in the first hyperpolarizabilities ($\beta$), with large (small) $\beta$ for $n=$odd ($n=$ even). Such odd-even oscillations have been reported experimentally on similar systems, but the origin of such phenomena has remained to be unclear. A detailed investigation about the origin of this odd-even oscillations based on conformation of the systems under study is presented in this part.

The second part comprises of the study on polymeric systems, based on para-nitroaniline (PNA), in which the alkyl spacers are placed on the two wings (hydrogens of NH$_2$ group were replaced with alkyl) of PNA. Number of alkyl groups, $n$, was changed from 1 to 7. Dynamic (ZINDO-SOS) and static (CPHF) theoretical calculations...
of polymers and the experimental evaluation of SHG efficiency have also been done, which agreed with the theoretical predictions.
PART-I
ODD-EVEN OSCILLATIONS IN THE FIRST
HYPERPOLARIZABILITY OF DIPOLAR
CHROMOPHORES: ROLE OF CONFORMATIONS OF
SPACERS

31.1. Introduction

In the field of nonlinear optics (NLO), π-conjugated systems have been a subject of intense study from both experimental and theoretical aspects.\textsuperscript{3-5} It is mainly because, the π-electrons are much easier to be excited with the application of laser field than the σ-electrons. Additionally, because of the large energy separation between the σ-and π-electrons in π-conjugated systems, there have been many theories based on purely π-electrons with σ-electrons forming the backbone. Although a more elaborate treatment would be necessary to include the all-electron picture, various effective semiempirical theories developed over the years have been used in a number of cases with reliable estimates of various properties including spectroscopic quantities.\textsuperscript{6} On the other hand, for systems with mainly σ-electrons or metallic clusters with very small π-σ separation, Hamiltonians consisting of all electrons in \textit{ab initio} level\textsuperscript{7} have gained enormous popularity in recent years.\textsuperscript{8,9} However, for large systems, the accurate determination of the excitation characteristics for dynamic spectroscopic applications still rely on semiempirical methods with configuration interactions.

In the present work, NLO properties have been calculated for a few dipolar chromophores that are separated by an alkyl bridge. The size of the alkyl group is varied to obtain an understanding of the orientation of the dipoles together with its effect on NLO properties of the system. The alkyl bridge acts as a harmless stitch, but, since it is flexible, leads to many different orientations in the dipoles. NLO properties of these systems have been calculated with a variation in the number of alkyl groups. The
observation is that for an even number of CH$_2$ spacers, the hyperpolarizabilities are much smaller than that for an odd number of CH$_2$ spacers. Thus, there is a manifestation of odd-even oscillation in the optical response functions. Such odd-even oscillations are well-known in the literature for many physical properties like the melting points of organic solids$^{10}$ and in the orientation of alkane thiol self-assembled monolayers (SAMs).$^{11}$ (Figure 31.1) Also, there have been recent reports of odd-even oscillations in NLO properties of organic molecules similar to those considered in the present work$^{12}$ and even in different molecular systems.$^{13}$

Figure 31.1. Schematic representation of orientation of SAMs depending on the number of spacers CH$_2$ (odd -even)

While oscillation in the physical properties such as melting point is generally understood on the basis of packing efficiencies in the van der Waal solids, oscillations in the electrical properties like hyperpolarizabilities are not quite well understood. The present work has been able to clearly show that such oscillations have their origin in the
conformational orientation of the spacers, thereby leading to different packing arrangements in solids or in thin films.

In this chapter, the discussion is about the molecular system considered and the conformational orientations of the spacers for a simple understanding of their energetics, followed by a description about the calculations of the first hyperpolarizability for systems with varying spacer length and explain the odd-even behavior based on the ground state and the excited-state dipole allowed transitions. Lastly, an analytical theory is developed to discuss the exciton splitting in these chromophores for various conformational angles.

31.2. Conformational flexibility

\[
\text{Figure 31.2} \quad \text{(A) Molecular structure of the system considered. (B) Orientation of the dipoles for odd and even numbered chains}
\]

Figure 31.2 shows the molecular system, bis(4-nitrophenylazo)diphenylmethane considered for the present study. All the geometries have been
optimized using the AM1 parameterized Hamiltonian available in the Gaussian 03 set of codes. The synthesis and characterization of a similar system, bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane is described in chapter 4. But a single crystal was not obtained. The geometries obtained by the AM1 calculations have been compared with geometries obtained using the DFT based methods at the B3LYP/6-31G+(d,p) level for the small sized chromophore with \( n = 2 \). It was found that the geometries obtained by both the methods have similar bond lengths and bond angles.

![Potential energy (in Kcal/mol) with twist along the central C-C single bond for \( n=2 \), solid line (circles), and \( n=12 \), dashed line (diamond)](image)

**Figure 31.3.** Potential energy (in Kcal/mol) with twist along the central C-C single bond for \( n=2 \), solid line (circles), and \( n=12 \), dashed line (diamond)

To further verify that the geometries do correspond to the global minima, the geometry for the experimental molecule, bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane was optimized. For this molecule also, the geometry as well as the interdipolar angle was similar to that considered for this study. Therefore, it is believed that the AM1 Hamiltonian is quite reliable for these systems and thus have proceeded with it for bigger systems with size up to \( n = 12 \). R-CH\(_2\)-CH\(_2\)-R, R = Ph-N=N-Ph-NO\(_2\), is the simplest symmetric case which can be considered to understand the
conformational orientations, as shown in Figure 31.2B. Rotation along the central C-C bond produces different geometries. For a torsional angle, $\phi = 0^\circ$, the situation corresponds to an eclipsed geometry while for $\phi = 180^\circ$, the conformation is staggered. In Figure 31.3, the potential energy profile for the system as the torsional angle is increased from $0^\circ$ to $180^\circ$ is plotted. The most stable point in the potential energy surface (PES) corresponds to $\phi = 180^\circ$ (staggered orientation in the dipoles) while the most unstable case is for $\phi = 0^\circ$ (the eclipsed form). Also, in the PES, there exists a local minimum between $\phi = 60^\circ$ and $80^\circ$ and a local maximum at $\phi = 120^\circ$. This is similar to the gauche butane interaction well-known in the literature. This arises due to the stronger nonbonding interaction between R and H at an angle of $\phi = 120^\circ$ compared to the weak R, R interaction in the gauche form at $\phi = 60^\circ$.

For $n=2$, the energy difference between the staggered and eclipsed form is 8 kcal/mol and that between the staggered and the gauche form is 1.04 kcal/mol. For comparison, the differences are 4.4-6.1 and 0.9 kcal/mol, respectively, for butane. For a longer chain, however, since there are more number of CH$_2$ groups, the degrees of freedom are much larger, allowing it to be in a state of random relaxed geometry without much constraints. In the same figure (Figure 31.3), the PES for the longest chain considered in the study, $n=12$ is also plotted. It is to be noted that for such a large methylene bridge there is no well-defined unique torsional angle parameter. However, for the sake of comparison, a twist along the central C-C bond, C (6)-C (7) was applied. It comparatively has a lower energy difference between the staggered and eclipsed form (6.5 kcal/mol) and between the staggered and gauche form (0.84 kcal/mol). For both $n = 2$ and $n = 12$, since the energy difference between the eclipsed and the staggered forms are more than the thermal energy at room temperature (0.6 kcal/mol), the staggered form is the most stable orientation for even numbered chain systems. It is also evident from the geometry optimized structures. However, since the gauche conformation lies at a local minimum, for longer chains this conformational form becomes thermally accessible. A gauche form is interesting because it induces helicity in a linear chain. Such helical chains being chiral exhibits good NLO responses for the even chains. It has been reported
for the poled films that the even numbered systems have good NLO responses, particularly for the longer chains.\textsuperscript{12} By this study it is believed that the origin of good NLO response functions in such even numbered chain systems is due to the presence of helical chains in a local minimum of the PES.

The odd numbered chains, however, show remarkable contrast. For the odd chains, the favorable arrangement corresponds to an eclipsed orientation for the dipoles, and there exists no local minimum conformation in the PES. This is explicitly shown in Figure 3I.2B. One can understand this phenomenon from the simple fact that all the alkyl units being in the sp\textsuperscript{3} environment introduces staggered geometry for all central units but eclipsed orientation at the extreme ends where the dipoles are located. So, the odd numbered chains will have an eclipsed orientation for the dipoles. For the even numbered chains, however, there is no such frustration in the dipole orientation, and all the units including the end dipoles remain staggered. Such a remarkable variation between the eclipsed and staggered conformation can be achieved by only changing the number of spacers between the dipoles.

3I.3. Optical response functions: role of spacer length

The geometries (Figure 3I.2A with varying n) obtained from the AM1 calculations were used to compute the SCF MO energies and then the spectroscopic properties using Zerner’s INDO method.\textsuperscript{20} The levels of CI calculations have been varied with singles (SCI) to obtain a reliable estimate of the second order optical response functions. The CI approach adopted here has been extensively used in earlier works and was found to provide excitation energies and dipole matrix elements in good agreement with experiment.\textsuperscript{21-23} For the Hartree-Fock determinant, varying number of occupied and unoccupied molecular orbitals were used to construct the CI space. To calculate the second-order NLO properties, correction vector method was used, which implicitly assumes all the excitations to be approximated by a correction vector (CV).\textsuperscript{24-28} The polarizabilities were also computed using the sum-over-states (SOS) formalism, and values similar to those provided by the CV method were obtained.
Table 31.1 gives the magnitudes of the ground-state dipole moment ($\mu_g$), oscillator strength ($f$), the optical gap ($\delta E$) [defined as the energy difference between the ground state and the lowest energy dipole allowed state], linear polarizability ($\alpha$), and first hyperpolarizability ($\beta$) for the molecules from $n=1$ to $n=12$. It is to be noted that the tumbling average quantities $\bar{\alpha}$ for the optical response functions are reported, which may be defined as

$$\bar{\alpha} = \frac{1}{3} \sum_i \alpha_i$$  \hspace{1cm} (31.1)

$$\bar{\beta} = \frac{1}{3} \sqrt{\sum_i \beta_i \beta_i^*}; \beta_i = \sum_j (\beta_{ij} + \beta_{ji} + \beta_{ji})$$  \hspace{1cm} (31.2)

Odd-Even Oscillations in First Hyperpolarizability of dipolar Chromophores: Role of Conformations of Spacers
where, the sums are over the coordinates \(x, y, z\) \((i, j = x, y, z)\) and \(\beta'\) refers to the conjugate of \(\beta\), vector. All the calculations have been performed at a frequency of 1064 nm \((1.67 \text{ eV})\) corresponding to the Nd:YAG laser. It is found that while the linear polarizability \(\alpha\) remains almost constant throughout the series \((\approx 155 \text{ esu})\), the ground-state dipole moment as well as the first hyperpolarizability \(\beta\) shows strong odd-even oscillations.

Specifically, \(\beta\) shows an order of magnitude increase for odd numbered chains compared to the even numbered chains. Furthermore, their values remain almost constant with the increase in the number of CH\(_2\) spacers \(n\), albeit for \(n = \text{odd}\) and \(n = \text{even}\) separately. The even numbered chains have very little dipole moment \((\approx 3 \text{D})\), while the odd ones have much higher dipole moment \((\approx 45 \text{D})\). The dipole moment was calculated for the single molecule, Ph-N=N-Ph-NO\(_2\), \(\mu_s = 39.20 \text{D}\). For a perfect parallel arrangement in the dipoles, the classical non-interacting picture predicts the total dipole moment as two times single chromophore value for parallel arrangement and zero for a perfect antiparallel arrangement. While, for the even numbered spacers the dipole moments are nearer to zero, the odd numbered spacers show a much smaller value from the classical result of twice the single chromophore value. Such a trend is easy to understand because, for the even numbered chains, the dipoles are staggered and almost perfectly antiparallel (Figure 31.3).
Figure 31.4. Frontier orbital plots for even and odd spacers. While the dipole moments are antiparallel for \( n = \text{even} \), \( n = \text{odd} \) have a finite angle 110°. The green arrow shows the direction of net dipole moment.

But, for the odd numbered chains, even though the orientations are eclipsed, the dipoles are not exactly parallel because of the sp\(^3\) hybridization along the alkyl principal axis. It is straightforward to calculate the angle (\( \phi \)) in which the dipoles are out of phase, using the classical dipole addition formula

\[
\mu_{\text{eff}}^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \phi.
\]

It is found that \( \phi \) has a magnitude of 110° for the odd chains. It is to be noted that although a classical dipole expression was used for finding the phase angle, it was a very good assumption as the saturated CH\(_2\) groups had very little electronic coupling with the \( \pi \) electrons in the either ends of the bridge. For example, the actual angle for the optimized molecule with \( n = 3 \) is 112°. The alkyl units basically act as a stitch between the two dipoles. This is illustrated with the frontier wave function plots for the chromophores. The HOMO, LUMO, and LUMO+1 in Figure 31.4 show no intermixing between the chromophores and thus behave independent of each other. (Within the one-electron picture, HOMO, LUMO, and LUMO+1 represent the ground state, the lowest one-photon state, and the two-photon states, respectively.) For cases as such, even the classical dipole interaction arguments are very accurate.
Figure 31.5. (a) Variation of inter chromophore distance, $d$ (in $\AA$), (b) first hyperpolarizability $\beta$ (in units of $10^{-30}$ esu), and (c) difference between the ground-state and the excited-state dipole moment, $\Delta \mu$ (in debye), with increase in the spacer length, $n$.

With the increase in the number of alkyl units, the distance between the dipoles increases. But, the distance between the even dipoles is more than their odd counterparts as the even ones have a centrosymmetric arrangement which increases their interchromophoric distances. Thus, the distance between the dipoles also exhibit an odd-even effect (Figure 31.5a). For each even distance, $\beta$ is small and for each odd distance, $\beta$ is large. Figure 31.5b shows the variation in the first hyperpolarizability $\beta$ with respect to the number of CH$_2$ units. Very similar to that for the ground-state dipole moment, $\beta$ also shows a prominent odd-even relation. For odd numbered chain, $\beta \approx 700$ while the even numbered chain have $\beta \approx 80$ (in units of $10^{-30}$ esu). The calculations are based on a CI basis with its dimension varying until a proper convergence is reached.

With in the framework of the two-state model, the second harmonic generation response (SHG) can be written as $^{29}$
$\beta_{\text{mon.-level}} = \frac{3e^2}{2\hbar} \frac{\omega_{12} f \Delta \mu}{(\omega_{12}^2 - \omega^2)(\omega_{12}^2 - 4\omega^2)}$  \hfill (31.3)

Where $\hbar \omega_{12}$ is the excitation energy, $f$ the oscillator strength, $\Delta \mu$ the difference between the dipole moments of the ground and the excited state and the $\omega$ specifies the excitation frequency of the oscillating electric field. The most important factor in the above expression is that the SHG coefficient is directly proportional to the oscillator strength $f$, and dipole moment difference, $\Delta \mu$ and is inversely proportional to the optical gap. Thus, any phenomenon that decreases the gap and increases the dipole moment difference between the ground and the excited state will enhance $\beta$. But as seen from Table 31.1 the optical gap ($\delta E$) remains almost constant along the series and shows no such odd-even oscillations. In fact, the oscillator strength for the even numbered chromophores is slightly larger than that for the odd ones. Thus, the only factor that governs such an odd-even oscillation is $\Delta \mu$. Figure 31.5c shows the variation of $\Delta \mu$ with increase with the spacer length. One can clearly see the odd-even variation in $\Delta \mu$ similar to that observed for $\beta$. This is to say that the excited state polarization has a strong dependence on the inter chromophoric arrangements.

31.4. Optical response functions: role of molecular conformation

From the discussion so far, it is evident that, one way to make parallel arrangement of dipoles is to connect the dipoles by an odd number of spacers. The conformation of the methylene itself forces such a parallel orientation. This methodology is elegant because CH$_2$ units being $\pi$-NLO inactive play no electronic role other than fine-tuning the conformational activity. But, at the same time, for even numbered chains, the stable conformers lead to an antiparallel arrangement of dipoles and thus the $\beta$ is less (in ideal cases, 0). So a proper understanding of the processes associated with this conformational change requires a more detailed analysis.
The simplest even numbered spacer system, $n = 2$, was considered and the variation of the ground-state and the excited-state properties was studied in relation to the variation of the dipolar angle ($\phi$). Figure 31.6a shows the variation in the ground-state dipole moment as the torsional angle is increased from $\phi = 0^\circ$ to $\phi = 180^\circ$. $\mu_g$ is a monotonically decreasing function and decays to zero at $\phi = 180^\circ$. It is to be noted that, for molecular system selected, the chromophores are not exactly planar, and thus there exists a small but finite dipole moment for staggered orientation. Additionally, $\phi$ is not $180^\circ$ for the optimized geometry. However, the antiparallel arrangement is similar in structure to that of the staggered optimized geometry.

For chromophoric aggregates separated by alkyl chains, there is no $\pi$-electron coupling between the bridge and the chromophores. This has also been verified from the
studies on oxo-bridged dinitroanilines. For such cases one can develop an analytical expression for the extent of exciton splitting due to the dipolar coupling between the organic chromophores. In the present molecular system, D-(CH₂)ₙ-D, the extent of the dipolar coupling between the two dipoles (named as _m_ and _n_ in the following equation) can be represented assuming purely electrostatic interaction between the dipoles as

\[
H_{mn} = \frac{\vec{M}_m \cdot \vec{M}_n}{r_{mn}^3} - \frac{3(M_m \cdot r_{mn})(M_n \cdot r_{mn})}{r_{mn}^4}
\]  

(31.4)

where \( \vec{M}_m \) is the transition dipole moment from state _i_ to state _j_ of a single dipolar unit and \( r_{mn} \) is the distance between the two molecular dipole centers, _m_ and _n_. It is to be noted that both the transition dipole and the distance \( (r_{mn}) \) in the numerator are vectorial quantities. Thus, the magnitude of the interaction term will depend crucially on the relative orientations of the dipolar molecules as well as on the axis joining their centers.

For the molecule under study, \( \phi \) is the angle between the planes of the dipolar molecules _m_ and _n_. \( \phi = 0^\circ \) represents the eclipsed dipolar arrangement while \( \phi = 180^\circ \) gives rise to a staggered dipolar arrangement. The dot product form of the above equation can be further simplified as

\[
H_{mn} = \frac{M_m^j}{r_{mn}^3} (\cos \phi - 3 \cos^2 \phi)
\]  

(31.5)
Figure 31.7. Schematic representation of the change in the optical gap due to twist along the C-C bond. Note that the smaller gap in the eclipsed form is due to the stability of the optically excited state together with destabilization of the ground state due to torsion ($E_{torso}$)

where $\theta$ is the angle made by the dipolar axis with the molecular axis. $R=\text{Ph-N=N-Ph-NO}_2$ is a quasi-1-D molecule, and thus the dipolar axis and the long molecular axis
coincides. $\theta$ is essentially zero in this case, giving rise to a simplified form for the coupling between the dipoles:

$$H_{mn} = \frac{M_y^2}{r_{mn}^3} (\cos \theta - 3)$$

(31.6)

Note that the $\theta$ term has a constant value and does not depend on the orientation of the spacers or the inter chromophoric arrangements. Therefore, even if $\theta$ is finite, it will give rise to a constant shift to the energies. From the simple tight binding Hamiltonian (in the limit of nearest-neighbor interactions only), the extent of the excitonic splitting associated with this dipolar coupling between the chromophores can be estimated to be $2H_{mn}$. Thus, the final expression for the splitting becomes:

$$\Delta E = 2 \frac{M_y^2}{r_{mn}^3} (\cos \theta - 3)$$

(31.7)

The distance $r_{mn}$ was calculated as the distance between the center of masses of the dipolar molecules as $\phi$ increases from $0^\circ$ to $180^\circ$. From the above analytical expression, it is clear that the extent of Frenkel exciton splitting decreases with increase in $\phi$, and thus the optical gap will increase. From the ZINDO calculations, exactly similar behavior was observed. Figure 31.6b shows the variation in the optical gap with increase in the angle $\phi$ from ZINDO calculations. As $\phi$ increases, the lowest excited state gets destabilized while the upper excited state becomes more stable, thereby increasing the optical gap. However, the gap saturates after $\phi \approx 80^\circ$. Both the numerator and the denominator ($r_{mn}^{-3}$) increase with the increase in $\phi$ as a result of which the gap saturates.

In Figure 31.6c, the variation of the oscillator strength ($f$) with respect to $\phi$ is shown. The oscillator strength for the dipole allowed state increases up to $\phi \approx 70^\circ$. However, with further increase in $\phi$, the oscillator strength remains constant. Figure
31.6d shows the variation of $\beta$ with respect to the interdipolar angle. $\beta$ is a decreasing function of $\phi$. However, the decrease is slow up to $\phi \approx 70^\circ$ and then decays rapidly with further increase in $\phi$.

Such a variation in $\beta$ can be well captured by the schematic process of exciton splitting shown in Figure 31.7. As $\phi$ increases from $0^\circ$ to $180^\circ$, the extent of excitonic splitting in the dipole allowed excited-state decreases, resulting in the increase in the optical gap (Figure 31.6b). (For the antiparallel arrangement of the dipoles, the transition occurs to the upper exciton state.) However, at the same time, this process leads to the stabilization of the ground state (from the eclipsed to the staggered form, Figure 31.3). It is to be noted that the ground-state energy is not a monotonically decreasing function and has a local maximum at $120^\circ$. But, the energy scale of the destabilization energy corresponding to the dipole allowed state is much higher ($0 - 0.5$ eV) than that for the conformational orientation stabilization of the ground state ($0.8$ kcal/mol), as $\phi$ is increased. Effectively thus, the optical gap (energy difference between the lowest dipole allowed state and the ground state) would increase with increase in $\phi$ from $0$. Both the two-state model and the full expression for $\beta$ have the optical gap in the denominator, and thus an increase in gap implies decrease in $\beta$. Additionally, with the increase in $\phi$, the oscillator strength ($f$) increases up to $\phi \approx 70^\circ$. Oscillator strength appears in the numerator of the $\beta$ expression, which explains the initial slow decrease of $\beta$ (Figure 31.6c).

31.5. Conclusions

To conclude, an extensive calculation on the effects of spacer length enhancement on the second-order NLO properties of dipolar molecules connected by CH$_2$ groups have been performed. $\beta$ shows a remarkable odd-even variation. For an odd number of spacers, the $\beta$ value is an order of magnitude higher than that for the even number of spacers. The origin for such oscillation is attributed to the similar oscillations in the dipole moment difference between the ground state and the dipole allowed state and to some extent on the variation in the oscillator strength. This arises due to the change in
the dipolar orientations between the staggered and eclipsed forms for the even and odd numbered chains, respectively.

From the present work, it is clear that this phenomenon of odd-even fluctuation in NLO properties is different from the variation of the physical properties like melting point in organic solids that have their origin in the van der Waals interactions among the solids where crystal packing is the most important parameter. It is also clear that the origin of odd-even oscillations is at the molecular scale. The energy analysis for the potential energy of twisting along the single bond shows that although the staggered form is the most stable conformation for the even numbered chains, but a thermally allowed local minimum exists between $\phi = 60^\circ$ and $80^\circ$, corresponding to the gauche form that will give rise to helicity in the chain. For example, for every 100 molecules in the staggered form, there are 18 molecules in the gauche form (Boltzmann distribution), and even for the $n = 2$ case, the Boltzmann-weighted average first hyperpolarizability, $\beta$, has a magnitude of $160.8 \times 10^{-30}$ esu. In the solid state, because of environment effects, the possibility of existence of such a helical form (local minimum) exists. As a result, for the even numbered chains, although a global minimum form ensures $\beta$ to be very small, supramolecular effects as in thin films will introduce appreciable $\beta$.

References


Odd-Even Oscillations in First Hyperpolarizability of dipolar Chromophores: Role of Conformations of Spacers


PART –II
SPACER EFFECT IN SHG OF POLYMERS CONTAINING AZOMESOGENS

3II.1. Introduction
In this part, a series of polymers were designed based on PNA. The polymers were designed as a condensation product of an azomesogen chromophore and a PNA derivative. The PNA derivative was designed by substituting the two hydrogens of NH₂ groups with alkyl spacers containing varying number of CH₂ from 1 to 7. The hyperpolarizability values, β were calculated by static (CPHF) and dynamic (ZINDO-SOS) method. Most of the polymeric systems were synthesized and SHG efficiency was measured experimentally.

3II.2. Monomer design
The route of monomer design is shown in Figure 3II.1.
The design starts with PNA. PNA (1) was condensed with dibromobutane (DBB, 2). The condensation product (PNADBB, 3) was reacted with diamines (4) varying from methylene diamine (Meth, \(n = 1\)) to heptyl diamine (Hept, \(n = 7\)). The product obtained contained the number of CH\(_2\) groups in the two wings of PNA which varied from 1 to 7 (Meth, Eth, Prop, But, Pent, Hex and Hept) to study the effect of alkyl spacer group in the value of \(\beta\) of the donor-acceptor system. All the monomer systems have been optimized with 6-31G basis sets using restricted Hartree-Fock formalism available in the Gaussian algorithm.\(^{14}\) The optimized geometries were used to compute the SCF MO energies. The static spectroscopic properties of monomers have been calculated using Coupled Perturbed Hartree-Fock (CPHF) method at RHF 6-31++G(d,p) level available in the Gaussian codes.\(^5\) The dynamic spectroscopic properties have been calculated using the Zerner's INDO SOS method with sum over 82 states.\(^{6,7}\)

3II.3. Hyperpolarizability \(\beta\) of monomers

The values of static Hyperpolarizability, \(\beta\) of monomers are given in Table 3II.1. It is clear that a small odd- even oscillation is observed in the ground state dipole moment \(\mu\) and Hyperpolarizability, \(\beta\) of these molecules (monomers) while the linear polarizability increases with the number of CH\(_2\) groups. The optimized structures for \(n=6\) (Hex) and \(n=7\) (Hept) are given in Figure 3II.2 and Figure.II.3. The parallel arrangement of dipoles in odd numbered chains and anti parallel arrangements of dipoles in even numbered chains are clear from the figure. As explained in part I of this chapter the odd- even oscillation in dipole moment, \(\mu\) and Hyperpolarizability, \(\beta\) is due to the molecular conformation of the chains. But in this case, the oscillations are not so visible and prominent due to the fact that the increment in CH\(_2\) groups has taken place simultaneously in the two wings of the PNA derivatives. Thus two end dipoles are always in parallel (eclipsed) arrangement irrespective of whether the chain is odd or even. This decreases the large change of \(\mu\) and \(\beta\) between the odd and even numbered chains. Also, in both cases, there was a common butyl unit in both wings of the molecule which contributes a non zero \(\mu\) and \(\beta\).
To compare with the results in part I of this chapter, the nonlinear properties of all the optimized structures have been calculated by dynamic ZINDO SOS calculations, the results are shown in Table 311.2. The dynamic calculation also agrees with the static calculations. Oscillator strength $f$, and Optical Gap $E$, were constant in this case also. The oscillation in $\Delta \mu$ is quite visible in this case. Even though there is a small odd-even oscillations, for $\mu$, and $\beta$, it is not visible as in the case of the system studied in part I. Figure 311.4 gives a comparative picture.

Table 311.1: HOMO-LUMO gap ($\Delta E$) in eV, Ground-State Dipole Moment ($\mu_0$) in Debye, Linear Polarizability ($\alpha$) in units of $10^{-23}$ esu, and First Hyperpolarizability $\beta$, in units of $10^{-30}$ esu for the chromophores (Ab initio CPHF static property calculations)

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>$\Delta E$</th>
<th>$\mu_0$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNA</td>
<td>0.3507</td>
<td>7.9627</td>
<td>1.35</td>
<td>8.94</td>
</tr>
<tr>
<td>DBB</td>
<td>0.4420</td>
<td>0.0005</td>
<td>1.25</td>
<td>1.06</td>
</tr>
<tr>
<td>PNADBB</td>
<td>0.4464</td>
<td>4.6995</td>
<td>2.99</td>
<td>1.38</td>
</tr>
<tr>
<td>Meth (n=1)</td>
<td>0.3968</td>
<td>8.5079</td>
<td>3.39</td>
<td>3.03</td>
</tr>
<tr>
<td>Eth (n=2)</td>
<td>0.3899</td>
<td>5.9852</td>
<td>3.76</td>
<td>2.56</td>
</tr>
<tr>
<td>Prop (n=3)</td>
<td>0.3911</td>
<td>8.7202</td>
<td>4.09</td>
<td>3.76</td>
</tr>
<tr>
<td>But (n=4)</td>
<td>0.3903</td>
<td>5.1224</td>
<td>4.43</td>
<td>3.40</td>
</tr>
<tr>
<td>Pent (n=5)</td>
<td>0.3902</td>
<td>8.7385</td>
<td>4.76</td>
<td>3.81</td>
</tr>
<tr>
<td>Hex (n=6)</td>
<td>0.3901</td>
<td>5.1218</td>
<td>5.10</td>
<td>3.41</td>
</tr>
<tr>
<td>Hept (n=7)</td>
<td>0.3900</td>
<td>8.1203</td>
<td>5.31</td>
<td>3.90</td>
</tr>
</tbody>
</table>

Figure 3.11.2. Optimized structure of Hex
Figure 3.11.3 Optimized structure of Hept

Table 3.11.2: Oscillator strength $f$, Optical Gap ($\Delta E$) in eV, Ground-State Dipole Moment ($\mu_0$) in debyes, Difference in dipole moment between ground state and excited state ($\Delta \mu$), Linear Polarizability ($\alpha$) in units of $10^{-21}$ esu, and First Hyperpolarizability $\beta$, in units of $10^{-6}$ esu for the chromophores (ZINDO SOS dynamic property calculations)

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>$f$</th>
<th>$\Delta E$</th>
<th>$\Delta \mu$</th>
<th>$\mu_0$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNA</td>
<td>1.0285</td>
<td>7.4823</td>
<td>14.1337</td>
<td>43.6312</td>
<td>2090</td>
<td>220.3553</td>
</tr>
<tr>
<td>DBB</td>
<td>0.1920</td>
<td>6.0458</td>
<td>47.6473</td>
<td>40.0614</td>
<td>1920</td>
<td>182.4640</td>
</tr>
<tr>
<td>PNADBB</td>
<td>0.2237</td>
<td>5.4948</td>
<td>36.4595</td>
<td>159.8493</td>
<td>7.67</td>
<td>631.5936</td>
</tr>
<tr>
<td>Meth(n=1)</td>
<td>0.6690</td>
<td>6.6234</td>
<td>21.9865</td>
<td>53.4916</td>
<td>1560</td>
<td>52.3075</td>
</tr>
<tr>
<td>Eth(n=2)</td>
<td>0.2641</td>
<td>4.8258</td>
<td>10.2105</td>
<td>40.9080</td>
<td>1570</td>
<td>51.5850</td>
</tr>
<tr>
<td>Prop(n=3)</td>
<td>0.2646</td>
<td>4.8253</td>
<td>21.1804</td>
<td>54.7053</td>
<td>1530</td>
<td>52.2516</td>
</tr>
<tr>
<td>But(n=4)</td>
<td>0.2644</td>
<td>4.8243</td>
<td>11.2536</td>
<td>31.7754</td>
<td>1530</td>
<td>52.0509</td>
</tr>
<tr>
<td>Pent(n=5)</td>
<td>0.2650</td>
<td>4.8240</td>
<td>21.2518</td>
<td>54.9802</td>
<td>1520</td>
<td>52.4288</td>
</tr>
<tr>
<td>Hex(n=6)</td>
<td>0.2654</td>
<td>4.8235</td>
<td>11.2372</td>
<td>31.7022</td>
<td>1500</td>
<td>51.8400</td>
</tr>
<tr>
<td>Hept(n=7)</td>
<td>0.2650</td>
<td>4.8233</td>
<td>21.2666</td>
<td>57.6567</td>
<td>1520</td>
<td>52.5469</td>
</tr>
</tbody>
</table>
Figure 3II.4. (a) Variation of difference between the ground-state and exited-state dipole moment, $\Delta \mu$ (in debye), (b) ground state dipole moment $\mu^g$ (in debye) (c) first hyperpolarizability $\beta$, with increase in the spacer length, $n$.

3II.4. Polymer design

The route of polymer design is shown in Figure 3II.5. The polymer was designed as a condensation product of previously designed PNA derivatives with...
varying number of spacers and an azomesogen chromophore, azobenzene-4, 4'-dicarbonyl chloride (AZCl). Thus a series of polymers with varying number of CH$_2$ groups from 1-7 in the polymer chain were designed.

\[ \text{Figure 3II.5 Route of polymer design} \]

All the polymer geometries (two repeating units) have been optimized using the AM1 parameterized Hamiltonian available in the Gaussian 03 set of codes. Static (CPHF) molecular properties of polymers have been calculated with 6-31 G (d) basis sets. The dynamic spectroscopic properties have been calculated using the Zerner's INDO SOS method with sum over 82 states. Optimized structure of two repeating unit is given in Figure 3II.6.
311.5. Hyperpolarizability $\beta$ of polymers

The values of static Hyperpolarizability, $\beta$, of polymers are given in Table 311.3. In the case of polymers designed from PNA derivatives with varying number of alkyl group, there is no visible odd-even oscillation in the ground state dipole moment and also in the value of first Hyperpolarizability $\beta$. While ground state dipole moment decreased randomly from Polmeth ($n=1$) to polhex ($n=7$), $\beta$ increased from Polmeth to Polhex. Closely examining the value of $\beta$, it can be seen that for every polymer chain containing even numbered spacer groups there is a slight decrease in the $\beta$ value. Hence, even though the odd-even oscillation is not much prominent in these types of polymeric systems, with respect to change in conformations of polymeric chains with odd or even numbered spacer groups, there is a small variation in $\beta$ value by virtue of having odd or even numbered spacer groups. The results from the dynamic ZINDO calculation also agree with this observation.
Table 3II.3: HOMO-LUMO (ΔE) in eV, Ground-State Dipole Moment (μ₀) in debye, Linear Polarizability (α) in units of 10⁻²¹ esu, and First Hyperpolarizability β, in units of 10⁻¹⁹ esu for the chromophores (ab initio CPHF static property calculations)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>ΔE</th>
<th>μ₀</th>
<th>α</th>
<th>β (static)</th>
<th>β (Dynamic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polmeth</td>
<td>0.3514</td>
<td>10.8861</td>
<td>8.70</td>
<td>1.40</td>
<td>632.4687</td>
</tr>
<tr>
<td>Poletl</td>
<td>0.3540</td>
<td>12.1547</td>
<td>9.01</td>
<td>1.32</td>
<td>493.3536</td>
</tr>
<tr>
<td>Polprop</td>
<td>0.3533</td>
<td>10.1751</td>
<td>9.23</td>
<td>5.25</td>
<td>627.5431</td>
</tr>
<tr>
<td>Polbut</td>
<td>0.3570</td>
<td>9.0564</td>
<td>9.65</td>
<td>4.77</td>
<td>493.3536</td>
</tr>
<tr>
<td>Polpent</td>
<td>0.3575</td>
<td>5.5329</td>
<td>9.98</td>
<td>6.05</td>
<td>627.5431</td>
</tr>
<tr>
<td>Polhex</td>
<td>0.3558</td>
<td>8.1486</td>
<td>10.20</td>
<td>5.54</td>
<td>504.6026</td>
</tr>
<tr>
<td>Polhept</td>
<td>0.3534</td>
<td>7.0044</td>
<td>10.40</td>
<td>7.30</td>
<td>625.6215</td>
</tr>
</tbody>
</table>

This can be explained as the addition effect of CH₂ spacer group in polymer chains. In spite of showing odd-even oscillations, polymer chains, have shown addition effect due to alkyl spacers in donor portion of the chain. These polymers the number of CH₂ groups were increased in both wings of the chain. Thus instead of an increment of one CH₂ in the polymer chains the increment was for two CH₂ spacer. This increases the push-pull mechanism of electron motion in polymer chain with increase in number of spacer and has shown an additive effect rather than an odd-even effect.

3II.6. Synthesis of monomers

3II.6.1. Synthesis of N,N-bis (4-bromobutyl)-4-nitrobenzenamine

Para-nitroaniline (1g, 0.00724 mol, s.d fine 99% pure) was dissolved in minimum amount of water. Sodium carbonate (1g, 0.00943 mol, s.d fine 98% pure) was added to this solution. The solution was kept under stirring on a magnetic stirrer. The temperature was kept at 98⁰ C. To this solution dibromobutane (4.23 ml, 0.0362 mol, Lancaster, 98% pure) was added drop wise from a pressure equalizing funnel and refluxed for 4 h under stirring. The reaction mixture was cooled and filtered. A brown solid was obtained. The precipitate was washed with water. Crystallized from ethanol. The crude product was purified by column chromatography using benzene and
benzene: ethyl acetate mixture. Bright yellow crystals of of N,N-bis (4-bromobutyl) -4 -nitrobenzenamine was obtained. Reaction scheme is given in Scheme 3II.1.

Scheme 3II.1 Synthesis of N,N-bis (4-bromobutyl) -4 -nitrobenzenamine

Characterization
Yield= 85% M.P. =160° C
Elemental analysis: Calculated for C14H12Br2N2O2 - C, 41.20; H, 4.94; N, 6.86. Found - C, 41.10; H, 4.98; N, 6.85
Spectral properties
UVλmax (solid) nm : 415
IR (KBr pellet) cm⁻¹: 1602 (C-N st) (1523 (NO₂ st as), 1476 (CH δ), 1441 (CH δ, of CH2-Br), 1324 (NO₂ stay) 1110 (C-Br st)
¹H NMR (300 MHz CDCl₃) δ : 8.10 (d, 2H, aromatic, H1), 6.45 (d, 2H, aromatic,H2), 3.42 (d, 4H, aliphatic H6), 3.40 (d, 4H, aliphatic H3), 2.07 (m, 4H aliphatic H5), 1.57 (m, 4H, aliphatic H4).
¹⁳C NMR (75 MHz CDCl₃) δ:152(aromatic, C1), 139(C4), 125 (aliphatic C2), 110 (aliphatic C3), 78 ( aliphatic C5), 41 (aliphatic C8), 36(aliphatic C7), 28(aliphatic C6).
Mass (m/e): 408 (molecular ion peak), 248 ( M-2Br), 220 ( O₂NC₆H₅N((CH₂)₃)₂.)
Figure 311.7. IR spectrum of N,N-bis (4-bromobutyl) -4 -nitrobenzenamine

Figure 311.8. $^1$H NMR spectrum of N,N-bis (4-bromobutyl) -4 -nitrobenzenamine
Figure 311.9 $^{13}$C NMR spectrum of N,N-bis (4-bromobutyl) -4-nitrobenzenamine

Figure 311.10 ESI Mass spectrum of N,N-bis (4-bromobutyl) -4-nitrobenzenamine

It is clear from the $^1$H NMR and $^{13}$C NMR spectra that disubstitution at NH$_2$ has occurred. If the product were a monosubstituted one, the aromatic region should have consisted of more number of peaks due to non equivalent protons in the aromatic
region. Also, there would have been a peak above δ4.0 due to unsubstituted H of NH₂. 8
different carbons in ¹³C NMR spectrum confirmed the disubstitution. If it were only
monosubstitution, there would have been 10 different carbons in the ¹³C NMR spectrum.

3II.6.2. Synthesis of N,N-bis (4-(2-aminoethylamino)butyl) -4 -nitrobenzenamine (eth)
N,N-bis (4-bromobutyl)-4-nitrobenzenamine (0.2g, 0.000491 mol) was dissolved
in THF. To this solution 60% NaH dispersion in paraffin oil (0. 0392g, 0.00491 mol, s. d.
fine) in THF was added drop wise using a pressure equalizing funnel. The solution was
kept at reflux. To this solution, 1, 2-diaminoethane (0.6 mL, 0.0098 mol, s. d. fine) in THF
was added drop wise and was refluxed for 6 h. Extraction with ether gave a brown
precipitate. The precipitate was washed with dil. HCl and distilled water. Dried and
recrystallized from ether. General route of synthesis is given in Scheme 3II.2
Yield 80%. M.P = 160°C. Elemental analysis: Calculated for C₁₅H₂₅N₄O₂ - C, 58.99; H,
9.35; N, 22.93. Found - C, 59.01; H, 9.40; N, 22.81
Spectral properties
UVλmax (solid) nm : 380
IR(KBr pellet) cm⁻¹ : 3500 (NH st), 2900, 2880 (2 sharp hydrogen bonded bands of NH₂
st), 1600 (NH₃ st, NH₂ st), 1530 (NO₂ st as), 1480 (NH₂ st), 1330 (NO₂ st ay)
¹H NMR (300 MHz CDCl₃) δ : 8.15 (d, 2H, aromatic hydrogen H1), 6.45 (d, 2H, aromatic
hydrogen H2), 3.41 (t, 4H aliphatic, H3), 2.95 (m, 8H, aliphatic H8 & H9), 2.62(t, 4H,
aliphatic H6), 2.15 (s, 4H, hydrogen of NH2), 1.75 (s, 2H, hydrogen of NH), 1.25 (m, 8H,
aliphatic H4 & H5)
¹³C NMR (75 MHz CDCl₃) δ: 146.0 (1C, aromatic carbon, C4), 136.5 (aromatic carbon
C1), 124.3 (2C, aromatic carbon, C2), 11.5 (2C, aromatic carbon, C3), 78.5, 77.3, 76.4 ( 1H,
aliphatic carbons C5, C8 & C9), 48.5 (1C, aliphatic carbon C10), 31.1 (1C aliphatic carbon
C7), 26.3( 1C aliphatic, carbon C6)
Mass (m/e): 366 (molecular ion), 251 (M- (CH₂)₄NH (CH₂)₄NH₂), 207 (O₂N₄H₅ (CH₂)₄
NH)
Scheme 3II.2 Synthesis of N,N-bis (4-(2-aminoethylamino)butyl) -4 -nitrobenzenamine

3II.6.3. Synthesis of N,N-bis (4-(3-aminopropylamino) butyl) -4 -nitrobenzenamine (prop)

N,N-bis (4-bromobutyl) -4 -nitrobenzenamine (0.2 g, 0.000491 mol) was dissolved in THF. To this solution 60% NaH dispersion in paraffin oil (0.04 g, 0.00491 mol) in THF was added drop wise using a pressure equalizing funnel. The solution was kept at reflux. To this solution 1, 3-diaminopropane (0.7 mL, 0.0098 mol, Lancaster, 98% pure) in THF was added drop wise and was refluxed for 6 h. Extraction with ether gave a brown precipitate. The precipitate was washed with dil. HCl and distilled water, dried and recrystallized from ether.

Yield 84%. M.P = 161.50° C. Elemental analysis: Calculated for C_{20}H_{38}N_{6}O_{2} - C, 60.88; H, 9.71; N, 21.71. Found - C, 60.40; H, 9.76; N, 21.10

Spectral properties

UV\text{\lambda}_{\text{max}} (solid) nm : 385
IR(KBr pellet) cm$^{-1}$: 3500 (NH st), 2950, 2875 (2 sharp hydrogen bonded bands of NH$_2$ st), 1625 (NH$_3$*5, NH'5), 1525 (NO$_2$ st as), 1450 (NH$_2$*5), 1320 (NO$_2$ st ay)

$^1$H NMR (300 MHz CDCl$_3$) $\delta$: 8.21 (d, 2H, aromatic hydrogen H1), 6.43 (d, 2H, aromatic hydrogen H2), 3.41 (t, 4H aliphatic, H3), 2.95 (m, 8H, aliphatic H8 & H9), 2.60 (t, 4H, aliphatic H6), 2.31 (s, 4H, hydrogen of NH$_2$), 1.85 (s, 2H, hydrogen of NH), 1.43 (m, 4H, hydrogen between H8 & H9), 1.25 (m, 8H, aliphatic H4 & H5)

$^{13}$C NMR (75 MHz CDCl$_3$) $\delta$: 146.1 (1C, aromatic carbon C4), 136.4 (aromatic carbon C1), 124.2 (2C, aromatic carbon, C2), 11.3 (2C, aromatic carbon C3), 78.5, 77.3, 76.4 (1H, aliphatic carbons C5, C8 & C9), 48.5 (1C, aliphatic carbon C10), 31.4 (1C aliphatic carbon C7), 30.5 (2C, aliphatic carbon between 9 & 10), 26.3 (1C, aliphatic carbon C6)

Mass (m/e): 394 (molecular ion), 265 (M- (CH$_2$)$_4$NH(CH$_2$)$_4$NH$_2$), 207 (O$_2$NCH$_3$ (CH$_2$)$_4$ NH)

III.6.4. Synthesis of N, N-bis (4-(4-aminobutylamino) butyl) -4 -nitrobenzenamine (but)

N,N-bis (4-bromobutyl) -4 -nitrobenzenamine (0.2g, 0.000491 mol) was dissolved in THF. To this solution 60% NaH dispersion in paraffin oil (0.0392g, 0.00491 mol) in THF was added drop wise using a pressure equalizing funnel. The solution was kept at reflux. To this solution, 1,4-diaminobutane (0.8 mL, 0.0098 mol, Lancaster, 98% pure) in THF was added drop wise and was refluxed for 6 h. Extraction with ether gave a brown precipitate. The precipitate was washed with dil. HCl and distilled water, dried and recrystallized from ether.

Yield 80%. M.P. = 159.91$^\circ$C. Elemental analysis: Calculated for C$_{22}$H$_{42}$N$_6$O$_2$ - C, 62.52; H, 10.02; N, 19.89. Found - C, 62.50; H, 10.0; N, 20.0

Spectral properties

UV$\lambda_{max}$ (solid) nm : 387

IR(KBr pellet) cm$^{-1}$: 3500 (NH st), 2700 (2 sharp hydrogen bonded bands of NH$_2$ st), 1600 (NH$_3$*8, NH'8), 1527 (NO$_2$ st as), 1480 (NH$_2$*8), 1330 (NO$_2$ st ay)

$^1$H NMR (300 MHz CDCl$_3$) $\delta$: 8.19 (d, 2H, aromatic hydrogen H1), 6.51 (d, 2H, aromatic hydrogen H2), 3.41 (t, 4H aliphatic, H3), 2.95 (m, 8H, aliphatic H8 & H9), 2.60 (t, 4H, aliphatic H6), 2.42 (s, 4H, hydrogen of NH$_2$), 2.01 (s, 2H, hydrogen of NH), 1.43 (m, 8H, hydrogens between H8 & H9), 1.30 (m, 8H, aliphatic H4 & H5)
Chapter 311

"C NMR (75 MHz CDCl₃) δ: 147.2 (1C, aromatic carbon C4), 136.7 (aromatic carbon C1), 1245.1 (2C, aromatic carbon, C2), 11.5 (2C, aromatic carbon C3), 78.5, 77.3, 76.4 (1H, aliphatic carbons C5, C8 & C9), 48.5 (1C, aliphatic carbon C10), 31.4 (1C aliphatic carbon C7), 30.7, 30.5, (2C, aliphatic carbons between 9 & 10) 26.3 (1C, aliphatic carbon C6)
Mass (m/e): 422 (molecular ion), 278 (M- (CH₂)₄ NH(CH)₆NI-I₂), 207 (O₂NC₆H₅ (CH₂)₄ NH)

311.6.5. Synthesis of N,N-bis (4-(6-aminohexylamino) butyl) -4 –nitrobenzenamine(hex)
N,N-bis (4-bromobutyl) -4 –nitrobenzenamine (0.2g, 0.000491 mol) was dissolved in THF. To this solution 60% NaH dispersion in paraffin oil (0. 0392g, 0.00491 mol) in THF was added drop wise using a pressure equalizing funnel. The solution was kept at reflux To this solution 1, 6-diaminohexane (1.0 mL, 0.0098 mol, Lancaster, 98% pure) in THF was added drop wise and was refluxed for 6 h. Extraction with ether gave a brown precipitate. Washed with dil. HCl and distilled water. Dried and recrystallized from ether.
Yield 79%. M.P = 160⁰ C. Elemental analysis: Calculated for C₂₅H₂₅N₆O₂ – C, 65.23; H, 10.53; N, 17.56. Found - C, 65.25; H, 10.50; N, 17.50
Spectral properties
UVλmax (solid) nm : 389
IR(KBr pellet) cm⁻¹: 3500 (NH st), 2925, 2850 (2 sharp hydrogen bonded bands of NH₂ st), 1600 (NH₂–, NH–), 1525 (NO₂ st as), 1480 (NH₂–), 1330 (NO₂ st ay)
¹H NMR (300 MHz CDCl₃) δ: 8.20 (d, 2H, aromatic hydrogen H1), 6.45 (d, 2H, aromatic hydrogen H2), 3.41 (t, 4H aliphatic, H3), 2.95 (m, 8H, aliphatic H₈ - H₉), 2.60(t, 4H, aliphatic H₆), 2.30 (s, 4H, hydrogen of NH₂), 1.87 (s, 2H, hydrogen of NH₇)1.44 (m,16H,hydrogen between H₈ & H₉), 1.28 (m, 8H, aliphatic H₄ & H₅)
¹³C NMR (75 MHz CDCl₃) δ:147.5 (1C, aromatic carbon C4), 136.9 (aromatic carbon C1), 124.1 (2C, aromatic carbon, C2), 11.9 (2C, aromatic carbon C3), 78.6, 77.0, 76.5 (1H, aliphatic carbons C5, C8 & C9), 48.9 (1C, aliphatic carbon C10), 31.2 (1C aliphatic carbon C7), 30.9, 30.3. 29.9 (2C, aliphatic carbons between 9 & 10), 26.3 (1C, aliphatic carbon C6)
Mass (m/e): 478 (molecular ion), 307 (M- (CH₂)₄ NH(CH)₆NH₂), 207 (O₂NC₆H₅ (CH₂)₄ NH)
3II.6.6. Synthesis of N,N-bis (4-(7-aminoheptylamino) butyl) -4 -nitrobenzenamine (hept)

N,N-bis (4-bromobutyl) -4 -nitrobenzenamine (0.2g, 0.000491 mol) was dissolved in THF. To this solution 60% NaH dispersion in paraffin oil (0. 0392g, 0.00491 mol) in THF was added drop wise using a pressure equalizing funnel. The solution was kept at reflux. To this solution, 1,7-diaminoheptane (1.2 mL, 0.0098 mol, Lancaster, 98% pure) in THF was added drop wise and was refluxed for 6h. Extraction with ether gave a brown precipitate. The precipitate was washed with dil. HCl and distilled water, dried and recrystallized from ether.

Yield 80%. M.P 161.24° C. Elemental analysis: Calculated for C_{33}H_{42}N_{6}O_{2} - C, 66.36; H, 10.74; N, 16.58. Found - C, 66.50; H, 10.60; N, 16.62

Spectral properties

UV\(\lambda_{max}\) (solid) nm : 392

IR(KBr pellet) cm\(^{-1}\) : 3500 (NH st), 2900, 2875(2 sharp hydrogen bonded bands of NH st), 1625 (NH\(_3\)\(^+\), NH\(^+\)\(^+\)), 1527 (NO\(_2\) st as), 1480 (NH\(_2\)\(^+\)), 1330 (NO\(_2\) st ay)

\(^1\)H NMR (300 MHz CDCl\(_3\)) \(\delta\) : 8.25 (d, 2H, aromatic hydrogen H1), 6.50 (d, 2H, aromatic hydrogen H2), 3.23 (t, 4H aliphatic, H3), 2.98 (m, 8H, aliphatic H8 & H9), 2.62(t, 4H, aliphatic H6), 2.51 (s, 4H, hydrogen of NH2), 1.95 (s, 2H, hydrogen of NH),1.45 (m,20H,hydrogen between H8 & H9), 1.31 (m, 8H, aliphatic H4 & H5)

\(^13\)C NMR (75 MHz CDCl\(_3\)) \(\delta\) : 147.3 (1C, aromatic carbon C4), 136.5 (aromatic carbon C1), 124.1 (2C, aromatic carbon, C2), 11.9 (2C, aromatic carbon C3), 78.8, 78.2, 76.5 (1H, aliphatic carbons C5, C8 & C9), 49.1 (1C, aliphatic carbon C10), 31.5 (1C aliphatic carbon C7), 30.8, 30.5, 29.9, 29.5 (2C, aliphatic carbons between 9 & 10) 26.3 (1C, aliphatic carbon C6)

Mass (m/e): 506 (molecular ion peak), 321 M- (CH\(_3\)\(_4\) NH(CH\(_2\))\(_7\)NH\(_2\)), 207 (O\(_2\)NC\(_6\)H\(_5\) (CH\(_3\))\(_2\)NH)
UV-Vis spectra of these compounds vary with increase in number of CH₂ groups from to 380-392. IR spectra (Figure 3II.11) have shown a sharp distinct doublet at δ 2900-2700 due to primary amine (NH₂ st) usually the doublet appears at δ 3500-3300 cm⁻¹. A lower wave number indicated presence of hydrogen bond.

In ¹H NMR spectra (Figure 3II.12) the aromatic region has only two type of hydrogens. It is because of 1,4-disubstitution which confirmed the dissubstitution of Br by diamines. Also the number of hydrogens with aliphatic region is also in good agreement with the dissubstitution. ¹³C NMR spectra (Figure 3II.13) gave additional proof for the proposed disubstituted structure. 4 carbons in the aromatic confirms the dissubstitution. Number of aliphatic carbons are also in good agreement with the proposed dissubstituted structure. Even numbered molecular ion (Figure 3II.14) confirms the presence of even number of nitrogen atom.
Figure 311.12 $^1$H NMR Spectrum of eth

Figure 311.13 $^{13}$C NMR Spectrum of eth
Synthesis of Polymers

All polymer syntheses were done in solution method at high temperatures. Appropriate PNA derivative was dissolved in extremely dry dimethylacetamide (HPLC, s.d fine). To this solution, azobenzene-4, 4'-dicarbonyl chloride (AZCl) dissolved in Ac was added. Few drops of extremely dry pyridine (99.99%, dry pyridine, 95%) were added as acid acceptor. The mixture was refluxed with stirring under nitrogen atmosphere for 24h. The product was precipitated from cold methanol and redissolved continuously with hot water, methanol and acetone. After filtration and drying, a solid was obtained. Scheme 311.3 gives the synthetic route of polymers.
Scheme 3II.3 Synthesis of polymers

**Poleth**: 4,4'-azobenzenedicarbonylchloride (0.083 g, 0.167 mol) and (N,N-bis (4-(2-aminooethylamino) butyl) -4 -nitrobenzenamine (0.2 g, 0.0005464 mol) were reacted. Yield: 87 %, \( T_g = 110.76^\circ C \), Initial decomposition temperature (IDT) = 265\(^\circ C \)

**Polprop**: 4,4'-azobenzenedicarbonylchloride (0.083 g, 0.167 mol) and (N,N-bis (4-(3-aminopropylamino) butyl) -4 -nitrobenzenamine (0.22 g, 0.0005464 mol) were reacted. Yield: 89 %, \( T_g = 93.42^\circ C \) IDT = 300\(^\circ C \)

**Polbut**: 4,4'-azobenzenedicarbonylchloride (0.083 g, 0.167 mol) and (N,N-bis (4-(4-aminobutylamino) butyl) -4 -nitrobenzenamine (0.23 g, 0.0005464 mol) were reacted. Yield: 86 % \( T_g = 95.43^\circ C \) IDT 308\(^\circ C \)

**Polhex**: 4,4'-azobenzenedicarbonylchloride (0.083 g, 0.167 mol) and (N,N-bis (4-(6-aminohexylamino) butyl) -4 -nitrobenzenamine (0.26 g, 0.0005464 mol) were reacted. Yield: 84 %, \( T_g = 99.35^\circ C \), IDT = 320\(^\circ C \)

**Polhept**: 4,4'-azobenzenedicarbonylchloride (0.083 g, 0.167 mol) and (N,N-bis (4-(7-aminohexylamino) butyl) -4 -nitrobenzenamine (0.28 g, 0.0005464 mol) were reacted.
Yield: 86 % Tg = 121.36° C, IDT 340° C

Spectral properties are similar for these polymers.

**Spectral properties of polymers**

UVλmax (solid) nm : 370-395

IR (KBr pellet) cm⁻¹ : 3426 (N-H st), 1684 (C=O, st, amide I), 1590 (C=O, st sy, amide II), 1522 (NO₂ st as), 1412 (N=N st), 1320 (NO₂ st sy), 1250 (N+N aromatic trans)

¹H NMR (300 MHz DMSO d₆)δ : 8.52 (d, aromatic hydrogen H12), 8.35 (d, aromatic hydrogen H11), 8.11 (d, aromatic hydrogen H1), 7.95 (s, hydrogen of NH H10), 6.89 (d, aromatic hydrogen H2), 4.53 (t, aliphatic hydrogen H3 & H9), 2.85 (t, aliphatic hydrogen H8), 2.54 (t, aliphatic hydrogen C6), 1.92 (s, hydrogen of NH H7), 1.34 (m, aliphatic hydrogens 4 & 5)

¹³C NMR (75 MHz DMSO d₆)δ: 167.6 (Carbonyl carbon C11), 156.1 (aromatic carbon C15), 155.7 (aromatic carbon C4), 137.9 (aromatic carbon C1), 136.4 (aromatic carbon C12), 127.8 (aromatic carbon C13), 123.1 (aromatic carbon C14), 122.0 (aromatic carbon C2), 115.3 (aromatic carbon C3), 51.1 (aliphatic carbon C5), 49.3, 48.9 (aliphatic carbon C8 & C9), 40.2 (aliphatic carbon C10), 28.3 (aliphatic carbon C7), 25.4 (aliphatic carbon C6)

From the Tg values and IDT, it can be seen that the polar order and stability increases with the increase in number of alkyl group in the polymer. The carbonyls peaks in IR (Figure 311.15) spectra at 1684 cm⁻¹ (amide I) and 1590 cm⁻¹ (amide II) indicated the presence of amide formation. In ¹H NMR spectra (Figure 311.16) four different types of hydrogen in the aromatic region confirmed the polymerization. The
shift of NH proton to a lower field (58) also confirmed the amide formation during the polymerization. The presence of carbonyl carbon in $^{13}$C NMR spectra (Figure 3II.17) confirmed the polymerization. Presence of 8 different carbon atoms in the aromatic region confirmed the proposed structure of polyamide. Mass spectrum of Polhept (Figure 3II.18) (molecular weight of one repeating unit =771) has shown the molecular ion peak at 6939 confirmed the proposed structure composed of nine repeating units.
3II.8. Evaluation of second harmonic generation efficiency

The NLO efficiencies of the polymers were determined with 2-methyl-4-nitroaniline as the standard using Kurtz and Perry method. Measurements were done by the powder method with a Quanta-Ray Nd-YAG laser from Spectra Physics (1064 nm, 10 ns, 365 mJ/S) integrated over 20 pulse and an average of 10 pulse. The samples were ground and graded with standard sieves to the phase matchable size (100-150 μm) and loaded on cuvette with 1mm thickness. MNA samples used as standards were also powdered and sieved (100-150 μm) after drying under high vacuum.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>SHG efficiency*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peleth</td>
<td>1.2371</td>
</tr>
<tr>
<td>Polprop</td>
<td>1.9689</td>
</tr>
<tr>
<td>Polbut</td>
<td>1.8091</td>
</tr>
<tr>
<td>Polhex</td>
<td>2.2856</td>
</tr>
<tr>
<td>Polhept</td>
<td>2.5346</td>
</tr>
</tbody>
</table>

*MAN SHG efficiency = 1
They were also mounted with the same thickness as the polymer samples. The laser beam was directed unfocused onto the sample kept at a 45° angle to the laser beam which provides the phase matchable situation; the emission was collected from the front face of the sample at 90° angle. The SHG signal at 532 nm was detected by Avantes 2048 spectrometer with CCD camera. The results are shown in Table 311.4.

From experimental measurements of SHG of polymers, it can be seen that the systems have shown increase in SHG efficiency with respect to increase in the number of alkyl spacer groups rather than showing an odd-even oscillation. In the polymer systems, at room temperature the molecules rotate randomly. In such case a restricted rotation about only one single bond is practically impossible. The molecules are rotating with respect to more than one bond. Therefore, the dipolar ends will rotate between the bonds and the population consists of a mixture of eclipsed and staggered conformation of dipolar ends (even though the ground state consists of more stable staggered conformations about a single bond). Under this circumstance, the additive effect of alkyl spacer group play the major role and the SHG efficiency increases with respect to the number of alkyl groups.

3III.9. Conclusion

By this work, it can be concluded that the odd-even oscillation of first Hyperpolarizability, $\beta$ has molecular origin. The conformation of dipolar ends governs the odd-even oscillations. From theory, it can be seen that in polymers, the odd-even oscillation is not visible due to the presence of more prominent additive effect of alkyl spacer groups. Experimental measurement of SHG of polymeric systems confirms this superiority of additive effect over odd-even oscillation of first Hyperpolarizability in the above explained polymer systems.

References

(3) Salahub, D. R.; Zerner, M. C. The Challenge of d and f Electrons; ACS: Washington
Chapter 311


Spacer Effect in SHG of Polymers Containing Azomesogens