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Odd−Even Oscillations in First Hyperpolarizability of Dipolar Chromophores: Role of Conformations of Spacers

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Quantum chemical calculations on the linear and nonlinear electric polarizabilities of dipolar molecules separated by the alkyl spacers have been performed on $O_2N-Ph-N{=}N-Ph-(CH_2)_n-Ph-N{=}N-Ph-NO_2$, $n = 1-12$. These molecules exhibit a very strong odd−even behavior in the first hyperpolarizabilities (β), with large (small) β for $n =$ odd ($n =$ even). Such odd−even oscillations have been reported experimentally on similar systems, but the origin of such phenomena remains unclear. We propose it to be due to the role of the conformational orientation of the intervening alkyl spacers that leads to eclipsed orientation (parallel) of the dipoles for $n =$ odd chains while staggered orientation (antiparallel) for $n =$ even chains. The energy difference between the two extreme angular forms is ≈6−8 kcal/mol, clearly more than the thermal fluctuations at room temperature. These conformational orientations will be preserved, leading to different packing arrangements at the macroscopic scale. We believe that it is this interaction at the molecular scale that controls such a macromolecular property.

1. Introduction

Tailoring the electronic and optical responses of materials for optical switching and all-optical processes is one of the areas of current interest in the field of nonlinear optics (NLO). In this context, materials based on organic molecules are most promising because of the ease with which they can be structurally manipulated to fine-tune their desired optical responses.[1] π-Conjugated systems have been a subject of intense study from both experimental and theoretical aspects.[2,3] It is mainly because the π-electrons are much easier to excite 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 accurate theories based on purely π-electrons with σ-electrons forming the backbone. Although a more elaborate treatment would be 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.[4] On the other hand, for systems with mainly σ-electrons or metallic clusters with very small $\sigma-\pi$ separation, Hamiltonians consisting of all electrons in ab initio level[5] have gained enormous popularity in recent years.[6,7] 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, we have calculated NLO properties of 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. These alkyl bridge act 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. We find 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 oscillations 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[8] and in the orientation of alkanethiol self-assembled monolayers (SAMs).[9] Also, there have been recent reports of odd−even oscillations in NLO properties of organic molecules similar to those considered in the present work[10] and even in different molecular systems.[11]

While oscillations 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. We have 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.

The paper is divided into five sections. In the next section we discuss the molecular system considered and the conformational orientations in the spacers for a simple understanding of their energetics. In section 3, we present 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. In the next section we develop an analytical theory to discuss the exciton

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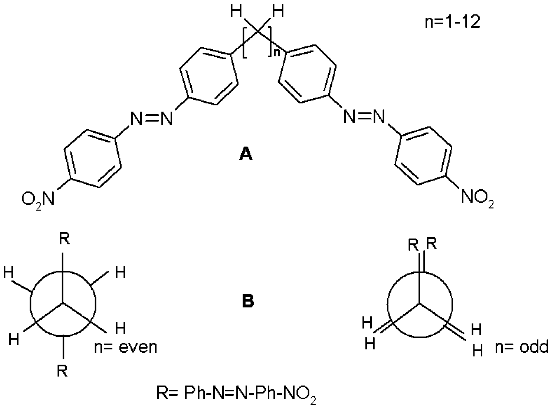

Figure 1. (A) Molecular structure of the system considered. (B) Orientation of the dipoles for odd and even chains.

splitting in these chromophores for various conformational angles. Finally, we conclude the paper with a summary in the last section.

2. Conformational Flexibility

Figure 1A shows the molecular system considered for the present study. All the geometries have been optimized using the AM1 parametrized Hamiltonian available in the Gaussian 03 set of codes.[12] Some of the compounds (with smaller alkyl units) have already been synthesized in good yields and well characterized by one of us although we have not been able to obtain a single crystal.[13] The geometries obtained by our AM1 calculations have been compared with geometries obtained using the DFT based methods at the B3LYP/6-31G+(d,p) level for the smaller sized chromophore with $n = 2$. We find that the geometries obtained by both the methods have similar bond lengths and bond angles. To further verify that the geometries do correspond to the global minima, we have optimized the geometry for the experimental molecule: 4,4′-diamino-2,2′-dinitrodiphenylmethane.[13] For this molecule also, the geometry as well as the interdipolar angle is similar to that considered for our study. Therefore, we believe 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 1B. Rotation along the central C−C bond produces different geometries. For a torsional angle, $\phi = 0°$, the situation corresponds to an eclipsed geometry while for $\phi = 180°$, the conformation is staggered. In Figure 2, the potential energy profile for the system as the torsional angle is increased from 0° to 180° is plotted. The most stable point in the potential energy surface (PES) corresponds to $\phi = 180°$ (staggered orientation in the dipoles) while the most unstable case is for $\phi = 0°$ (the eclipsed form). Also, in the PES, there exists a local minima between $\phi = 60°$ and 80° and a local maxima at $\phi = 120°$. This is similar to the *gauche* butane interaction well-known in the literature.[14] This arises due to the stronger nonbonding interaction between R and H at an angle of $\phi = 120°$ compared to the weak R, R interaction in the gauche form at $\phi \approx 60°$.

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.[15] 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 2), we also plot the PES for the longest chain considered in the work: $n = 12$. Note that for such a large methylene bridge there is no well-defined unique torsional angle parameter. However, for the sake of comparison, we twist along the central C−C bond, C(6)−C(7). 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 chain systems. It is also evident from the geometry optimized structures. However, since the gauche conformation lies at a local minima, 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.[16−18] It has been reported for the poled films that the even systems have good NLO responses, particularly for the longer chains.[10] We believe that the origin of good NLO response functions in such even chain systems is due to the presence of helical chains in a local minima of the PES.

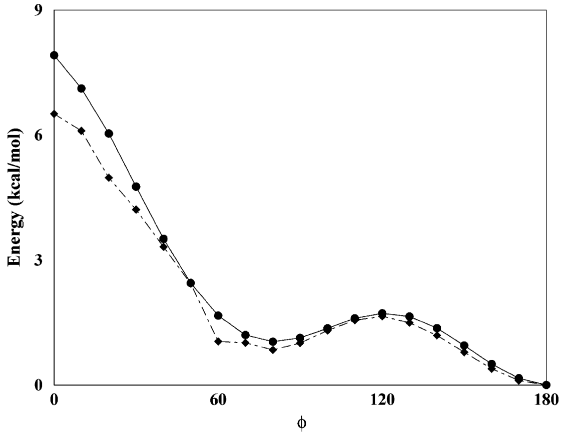

Figure 2. Potential energy (in kcal/mol) with twist along the central C−C single bond: for $n = 2$, solid line (circles), and $n = 12$, dashed line (diamond).

The odd 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 minima conformation in the PES. This is explicitly shown in Figure 1B. One can understand this phenomenon from the simple fact that all the alkyl units being in the sp^3 environment introduces staggered geometry for all central units but eclipsed orientation at the extreme ends where the dipoles are located. So, the odd chains will have a staggered orientation for the dipoles. For the even chains, however, there is no such frustration in the dipole orientations, 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.

3. Optical Response Functions: Role of Spacer Length

The geometries (Figure 1A 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.[19] 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

TABLE 1: Oscillator Strength (*f*), Optical Gap (δE) in eV, Ground-State Dipole Moment (μ_G) in debye, Linear Polarizability (α) in Units of 10^{-24} esu, and First Hyperpolarizability β in Units of 10^{-30} esu for the Chromophores in Figure 1A, with Increase in Spacer Length

spacer	f	δE	μ_G	α	β
$n = 1$	2.01	4.25	44.40	1500.48	537.06
$n = 2$	2.59	4.42	3.02	1561.44	73.03
$n = 3$	1.78	4.34	46.32	1475.04	614.24
$n = 4$	2.52	4.43	3.36	1560.96	50.91
$n = 5$	1.72	4.43	45.12	1539.36	647.88
$n = 6$	2.50	4.43	3.58	1556.64	48.38
$n = 7$	1.82	4.44	42.34	1488.96	813.08
$n = 8$	2.66	4.46	3.50	1490.88	93.31
$n = 9$	1.56	4.43	47.47	1540.8	636.36
$n = 10$	1.83	4.43	2.35	1555.2	70.73
$n = 11$	1.62	4.43	43.73	1610.4	594.89
$n = 12$	1.84	4.43	3.84	1618.56	73.26

provide excitation energies and dipole matrix elements in good agreement with experiment.[20-22] For the Hartree−Fock determinant, we use varying number of occupied and unoccupied molecular orbitals to construct the CI space. To calculate the second-order NLO properties, we use correction vector method, which implicitly assumes all the excitations to be approximated by a correction vector (CV).[23-26] The polarizabilities were also computed using the sum-over-states (SOS) formalism, and values similar to those provided by the CV method were obtained.

In Table 1. we report the magnitudes of the ground-state dipole moment (μ_G), oscillator strength (*f*), the optical gap (δE) [defined as the energy difference between the ground state and the lowest energy dipole allowed state], linear polarizability (α), and first hyperpolarizability (β) for the molecules from $n = 1$ to $n = 12$. Note that we report the tumbling average quantities[27] for the optical response functions, defined as

$$\bar{\alpha} = \frac{1}{3}\sum_i (\alpha_{ii})$$

$$\bar{\beta} = \sqrt{\sum_i \beta_i \beta_i^*};\quad \beta_i = \frac{1}{3}\sum_j (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \qquad (1)$$

where the sums are over the coordinates x, y, z ($i, j = x, y, z$) and β_i^* refers to the conjugate of β_i vector. All the calculations have been performed at a frequency of 1064 nm (1.67 eV) corresponding to the Nd:YAG laser. We find that while the linear polarizability (α) remains almost constant throughout the series (≈1550), the ground-state dipole moment as well as the first hyperpolarizability (β) shows strong odd−even oscillations. Specifically, β shows an order of magnitude increase for odd chains compared to the even chains. Furthermore, their values remain almost constant with the increase in the number of CH_2 spacers n, albeit for n = odd and n = even separately.

The even chains have very little dipole moment (≈3 D) while the odd ones have much higher dipole moment (≈45 D). We have calculated the dipole moment for the single molecule, Ph−N=N−Ph−NO_2, $\mu_G \approx 39.20$ D. For a perfect parallel arrangement in the dipoles, the classical noninteracting picture predicts the total dipole moment as 2× single chromophore value for parallel arrangement and 0 for a perfect antiparallel arrangement. While, for the even spacers the dipole moments are nearer to zero, the odd 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 chains the dipoles are staggered and almost perfectly antiparallel (see Figure 3). But, for the odd 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 (ϕ) in which the dipoles are out of phase, using the classical dipole addition formula $\mu_{\text{eff}}^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\phi$. We find that ϕ has a magnitude of 110° for the odd chains. Note that although we are using a classical dipole expression for finding the phase angle, it is a very good assumption as the saturated CH_2 groups have very little electronic coupling with the π-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+1, and LUMO+2[28] in Figure 3 show no intermixing between the chromophores and thus behave independent of each other. For cases as such, even the classical dipole interaction arguments are very accurate.

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 4a). For each even distance, β is smaller and for each odd distance, β is larger. Figure 4b shows the variation in the first hyperpolarizability β with respect to the number of CH_2 units. Very similar to that for the ground-state dipole moment, β also shows a very prominent odd−even relation. For odd chain, $\beta \approx 700$ while the even chain have $\beta \approx 80$ (in units of 10^{-30} esu). Our calculations are based on a CI basis with its dimension varying until a proper convergence is reached.

Within the framework of the two-state model, the second harmonic generation response (SHG) can be written as[29]

$$\beta_{\text{two-level}} = \frac{3e^2}{2\hbar}\frac{\omega_{12} f \Delta\mu}{(\omega_{12}^2 - \omega^2)(\omega_{12}^2 - 4\omega^2)} \qquad (2)$$

where $\hbar\omega_{12}$ is the excitation energy, f is the oscillator strength, $\Delta\mu$ is the difference between the dipole moments of the ground and the excited state, and ω specifies the excitation frequency of the oscillating electric field. The most important factor in the above simple expression is that the SHG coefficient is directly proportional to the oscillator strength and the dipole moment difference and is inversely proportional to the optical gap. Thus, any phenomenon that decreases the gap or increases the dipole moment difference between the ground and the excited state or increases the oscillator strength will enhance β. But as seen from Table 1, the optical gap (δE) remains almost constant along the series and shows no such odd−even oscillations. In fact, the oscillator strength for the even 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 4c shows the variation of $\Delta\mu$ with increase in the spacer length. One can clearly see the odd−even variation in $\Delta\mu$ similar to that observed for β. This is to say that the excited-state polarization has a strong dependence on the interchromophoric arrangements.

4. Optical Response Functions: Role of Molecular Conformations

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

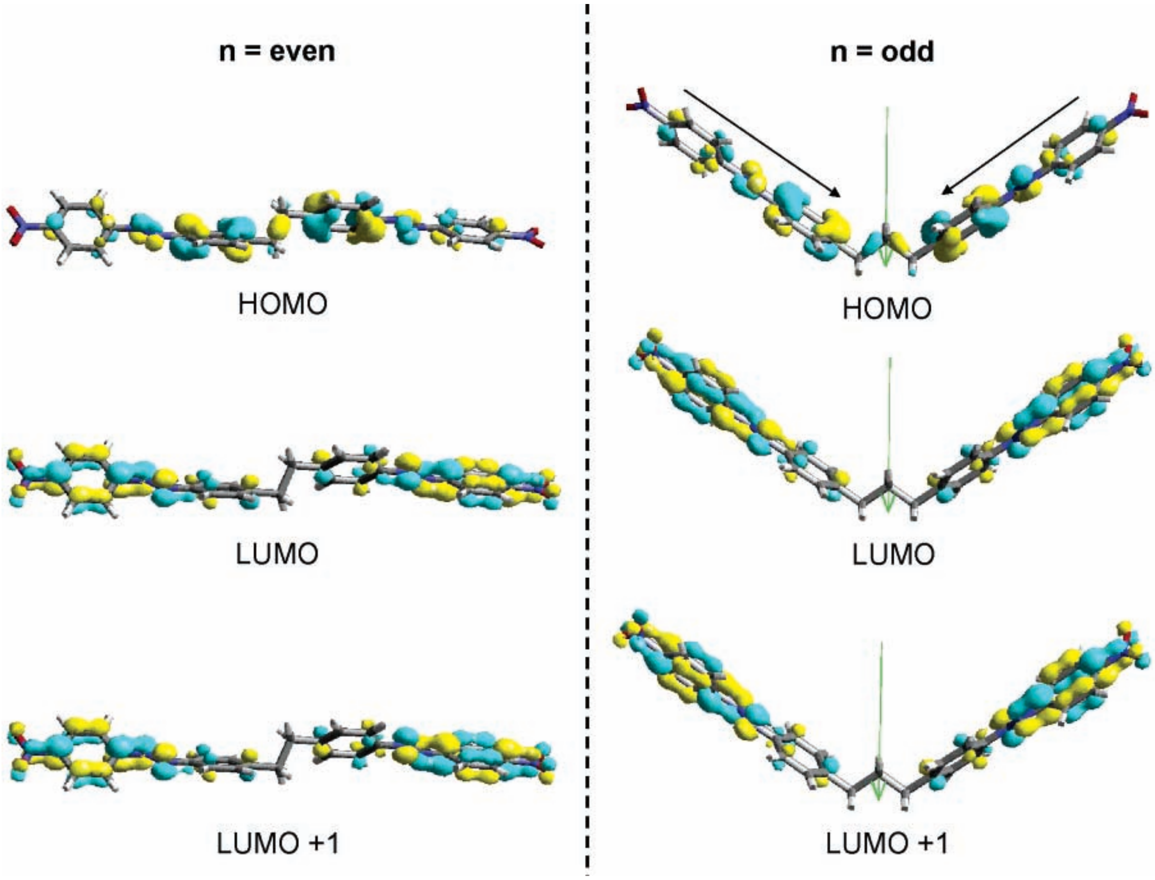

Figure 3. Frontier orbital plots for even and odd spacers. While, the dipoles are antiparallel for n = even, n = odd have a finite angle (110°). The green arrow shows the direction of the net dipole moment.

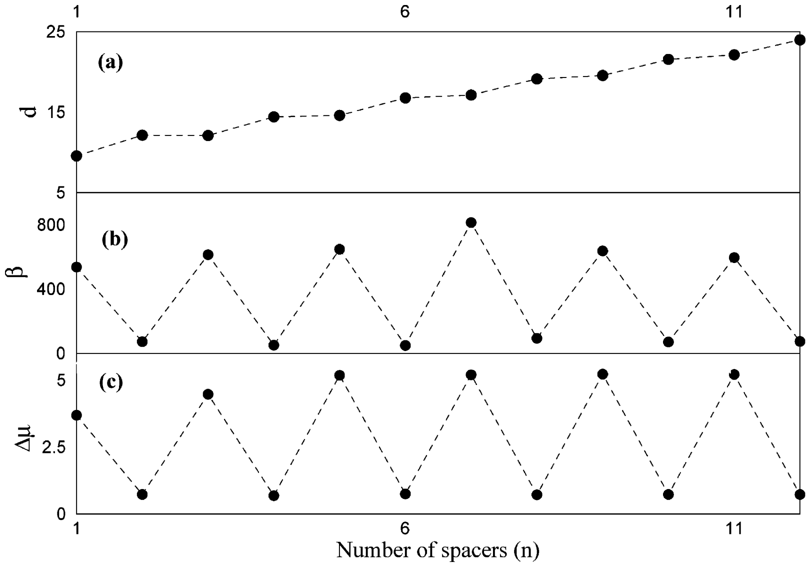

Figure 4. (a) Variation of interchromophore distance, d (in Å), (b) first hyperpolarizability β (in units of 10^{-30} esu), and (c) difference between the ground-state and the excited-state dipole moment, $\Delta\mu$ (in debye), with the increase in the spacers length, n.

forces such a parallel orientation. This methodology is elegant because CH_2 units being π-NLO inactive play no electronic role other than fine-tuning the conformational activity. But, at the same time for even chains, the stable conformers lead to an antiparallel arrangement of dipoles and thus the β is less (in ideal cases, 0). So a proper understanding of the processes associated with this conformational change requires a more detailed analysis.

We consider the simplest even spacer system, $n = 2$, and study the variation of the ground-state and the excited-state properties with the variation of the dipolar angle (ϕ). Figure 5a shows the variation in the ground-state dipole moment as the torsional angle is increased from ($\phi = 0°$ to $\phi = 180°$). μ_G is a monotonically decreasing function and decays to zero at $\phi = 180°$. Note that, for our molecular system, the chromophores are not exactly planar, and thus there exists a small but finite dipole moment for staggered orientation. Additionally, ϕ is not 180° for the optimized geometry. However, the antiparallel arrangement is similar in structure to that of the staggered optimized geometry.

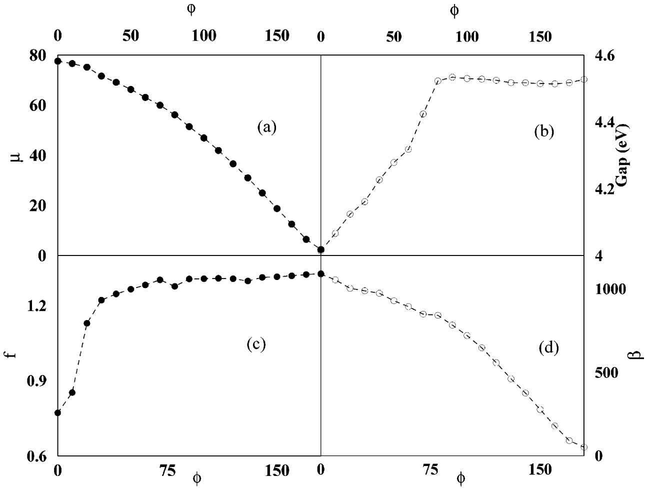

Figure 5. Variation of (a) ground-state dipole moment μ_G (in debye), (b) optical gap (in eV), (c) oscillator strength (*f*) of the dipole-allowed states, and (d) first hyperpolarizability β (in 10^{-30} esu), with the torsional angle, ϕ, from ZINDO calculations.

For chromophoric aggregates separated by alkyl chains, there is no π-electron coupling between the bridge and the chromophores. This has also been verified from our previous studies on oxo-bridged dinitroanilines.[30] 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$-$(CH$_2$)$_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

$$H_{m,n} = \frac{\vec{M}_{ij}\cdot\vec{M}_{ij}}{r_{mn}^{3}} - \frac{3(\vec{M}_{ij}\cdot\vec{r}_{mn})(\vec{M}_{ij}\cdot\vec{r}_{mn})}{r_{mn}^{5}} \qquad (3)$$

where $\vec{M}_{ij}$ 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 ($\vec{r}_{mn}$) 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, ϕ is the angle between the planes of the dipolar molecules *m* and *n*. $\phi = 0°$ represents the eclipsed dipolar arrangement while $\phi = 180°$ gives rise to a staggered dipolar arrangement. The dot product form of the above equation can be further simplified as

$$H_{m,n} = \frac{M_{ij}^{\ 2}}{r_{mn}^{\ 3}}(\cos\phi - 3\cos^2\theta) \qquad (4)$$

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

$$H_{m,n} = \frac{M_{ij}^{\ 2}}{r_{mn}^{\ 3}}(\cos\phi - 3) \qquad (5)$$

Note that the θ term has a constant value and does not depend on the orientation of the spacers or the interchromophoric arrangements. Therefore, even if θ 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 $2H_{m,n}$.[31] Thus, the final expression for the splitting becomes

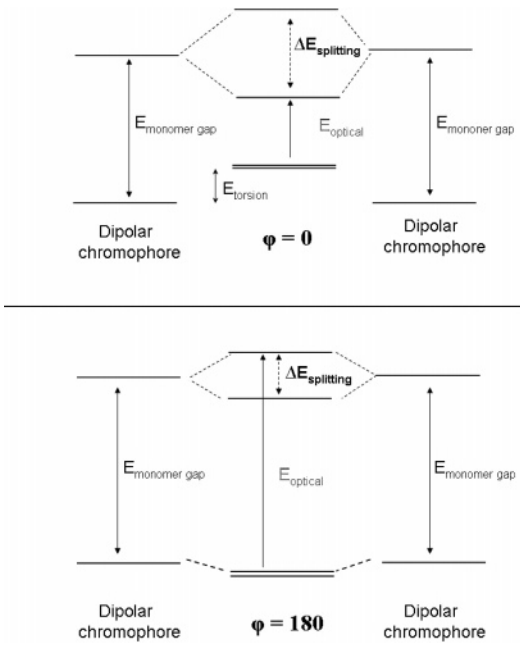

Figure 6. Schematic representation of the change in the optical gap due to twist along the C$-$C bond. Note that the smaller gap in the eclipsed form is due the stability of the optically excited state together with destabilization of the ground state due to torsion (E_{torsion}).

$$\Delta E = 2\,\frac{M_{ij}^{\ 2}}{r_{mn}^{\ 3}}(\cos\phi - 3) \qquad (6)$$

We calculate the distance r_{mn} as the distance between the center of masses of the dipolar molecules as ϕ increases from 0° to 180°. From the above analytical expression, it is clear that the extent of Frenkel exciton splitting decreases with increase in ϕ, and thus the optical gap will increase. From our ZINDO calculations, we find exactly similar behavior. Figure 5b shows the variation in the optical gap with increase in the angle ϕ from ZINDO calculations. As ϕ 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 $\phi \approx 80°$. Both the numerator and the denominator ($r_{mn}^{\ 3}$) increase with the increase in ϕ as a result of which the gap saturates.

In Figure 5c, the variation of the oscillator strength (*f*) with respect to ϕ is shown. The oscillator strength for the dipole allowed state increases up to $\phi \approx 70°$. However, with further increase in ϕ, the oscillator strength remains constant. Figure 5d shows the variation of β with respect to the interdipolar angle. β is a decreasing function of ϕ. However, the decrease is slow up to $\phi \approx 70°$ and then decays rapidly with further increase in ϕ.

Such a variation in β can be well captured by the schematic process of exciton splitting shown in Figure 6. As ϕ increases from 0° to 180°, the extent of excitonic splitting in the dipole allowed excited-state decreases, resulting in the increase in the optical gap (Figure 5b). (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, see Figure 2). Note that the ground-state energy is not a monotonically decreasing function and has a local maxima at 120°. 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 ϕ is increased. Effectively thus, the optical gap (energy difference between the lowest dipole allowed state and the ground state) would increase with increase in ϕ from 0. Both the two-state model and the full expression for β have the optical gap in the denominator, and thus an increase in gap implies decrease in β. Additionally, with the increase in ϕ, the oscillator strength (f) increases up to $\phi \approx 70°$. Oscillator strength appears in the numerator of the β expression, which explains the initial slow decrease of β (Figure 5c).

5. Conclusions

To conclude, we have performed an extensive calculation on the effects of spacer length enhancement on the second-order NLO properties of dipolar molecules connected by the CH_2 groups. β shows a remarkable odd−even variation. For an odd number of spacers, the β 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 form for the even and odd 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. The energy analysis for the potential energy of twisting along the single bond shows that although the staggered form is the most stable geometry for the even chains but a thermally allowed local minimal exists between $\phi = 60°$ and 80°, 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, β, has a magnitude of 160.8×10^{-30} esu. In the solid state, because of environment effects, the possibility of existence of such a helical form (local minimal) exists. As a result, for the even chains although a global minimum form ensures β to be very small, supramolecular effects as in thin films will introduce appreciable β.

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