

Hyperpolarizability studies of some nonconjugated twin donor–acceptor molecules

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Abstract. Extensive theoretical calculation on the effects of spacer length enhancement on the second-order NLO properties of twin donor acceptor molecules having two amide units bridged by the CH₂ spacers was performed. The role of such aliphatic bridges on the Donor–Acceptor groups was computed by ZINDO/CV quantum chemical formalism. The odd-even effects were observed in twin donor acceptor systems (with two aliphatic units) linked by an alkyl spacer of varying length from $n = 1$ to $n = 12$. The system considered for the present study was N,N' -alkane-(1, n) diyl *bis*-4-hydroxy hexanamides. For an odd number of CH₂ spacers, the β value was an order of magnitude higher than that for the even number of CH₂ 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.

Keywords. Nonlinear optics; oscillator strength; optical gap; polarizability.

1. Introduction

The design of materials with large nonlinear optical (NLO) responses has been a topic of active research because of their potential applications in a number of advanced optoelectronic devices (Pal *et al* 2008). The development of organic second-order NLO materials is motivated by the promising performance and cost improvements related to telecommunications, computing, embedded network sensing, signal transmission, and many other optical applications (Park *et al* 2004). It is well-known that second-order NLO properties originate from the noncentrosymmetric alignment of NLO chromophores (generally achieved under an electric field), either doped as a guest or covalently introduced to the polymer systems, although the strong intermolecular dipole–dipole interactions among the chromophore moieties in the polymeric system make the poling-induced noncentrosymmetric alignment of chromophores a daunting task (Li *et al* 2009).

Nonlinear optics deals with the interaction of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields. When a beam of light is impinged on a material it causes the charges of the atom to oscillate. In a linear material the amount of charge displacement is proportional to the instantaneous magnitude of the electric field. The charges oscillate at

the same frequency as the incident light. The oscillating charges either radiate light at that frequency or the energy is transferred into non-radiative modes that result in material heating or other energy transfer mechanisms. With small fields the displacement of charge from the equilibrium position, polarization (P), will be proportional to the applied field, E .

$$P = \alpha E, \quad (1)$$

where α is the linear polarizability.

In a nonlinear optical material, the displacement of charge from its equilibrium value is a nonlinear function of the electric field. When exposed to laser light, i.e. very high intensity electric field, the polarizability of all materials can be drawn beyond a linear regime (Gunter 2000; Robert and Boyd 2009).

Nonlinear polarization

$$P = P_0 + \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots \quad (2)$$

In this paper, a theoretical analysis of the nonlinear optical properties of the twin donor acceptor systems is presented using the established ZINDO (SOS)/CV quantum chemical formalism. Even though, *ab initio*-CPHF computations are numerically more accurate and precise, the results are not easily amenable to chemical interpretation. Since they are based on derivative rather than SOS formalism, the interpretation of computed response is difficult, albeit of their accuracy in predicting trends. Also, in experimental measurements, electrons will go to the higher excited states and the higher level contribution may not be too small to neglect. Almost all the semiem-

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pirical SOS procedures provide second order responses in reasonable agreement with experiments. Moreover, they permit a basic understanding of the origin of the NLO response in a chemical sense, by identifying the molecular excited states primarily responsible for an NLO response within the SOS formalism (Kanis *et al* 1994).

2. Twin D–A system for NLO study

The molecular systems considered for the NLO study were the amido diols which were experimentally synthesized by the aminolysis of ϵ -caprolactone by using the diamino alkanes (Guass 2000). The electron acceptor groups and donor groups were attached to a non-conjugated system and the donor-acceptor systems show charge transfer between electron donating and electron withdrawing groups and hence develop the polarization in the system. By designing the effective NLO chromophores (highly active chromophore molecules which have a large molecular hyperpolarizability β), which can be incorporated into a polymer chain either in the main chain or side chain by covalent linkages one could develop polymer systems with high second harmonic generation efficiency. The twin donor-acceptor system ($D-A-A-D$) and single donor-acceptor system ($D-A$) selected for the NLO study are shown in the figure 1.

In this article we have tried to examine the dipole moment, polarizability, hyperpolarizability, oscillator strength and optical gaps of the twin donor acceptor systems by varying the number of alkyl groups between $D-A$ and $A-D$ chromophores.

3. Methodology

Figure 1 shows the molecular systems considered for the present study. All the geometries have been optimized using the AM1 parametrized Hamiltonian available in the Gaussian 03 set of codes (Guass 2000; Yongjun *et al* 2000; Gaussian 2003). Some of the compounds (with smaller alkyl units) have already been synthesized in good yields and well characterized (Elizabeth and Sreekumar 2008). The geometries obtained by the AM1 calculations have been compared with geometries obtained using the

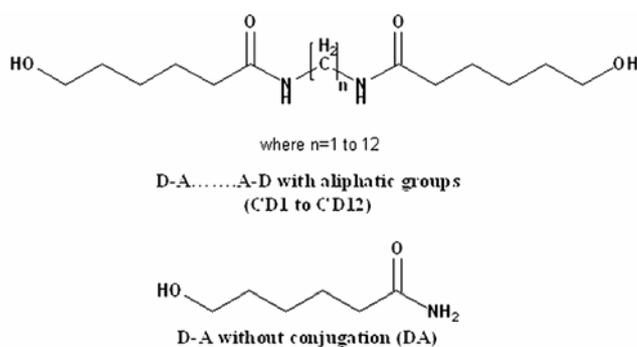


Figure 1. Twin donor acceptor systems.

HF based methods for the smaller chromophore with $n = 2$. The geometries obtained by the HF and AM1 methods have similar bond lengths and bond angles. 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 $n = 12$. These optimized geometries were used to compute the NLO properties using the Zerner's INDO method (Datta and Pati 2005a; Davis *et al* 2005). The level of CI calculations, were taken with singles (SCI) to obtain a reliable estimate of the second order optical response. The reference determinants chosen are dominant in the description of the ground state and the lowest one-photon excited states. For each reference determinant, 8 occupied and 8 unoccupied molecular orbitals were used to construct a CI space with configuration dimension of 900. To calculate NLO properties, the correction vector method was used, which implicitly assumes all the excitations to be approximated by a correction vector (Datta and Pati 2005b; Dewar *et al* 1985). The CI approach adopted here has been extensively used in earlier works and provided excitation energies and dipole matrix elements in good agreement with experiment. The polarizabilities were also computed using the sum-over-states (SOS) formalism, and values similar to those provided by the CV method were obtained. All the calculations have been performed at a frequency of 1064 nm (1.17 eV) corresponding to the Nd:YAG laser. Details of this method have been published in a number of papers (Albert and Ramasesha 1990; Ramasesha and Albert 1990; Ramasesha *et al* 1995; Datta and Pati 2004, 2005a, 2006).

4. Results and discussion

The change in dipole moment ($\Delta\mu$) (the difference in dipole moments between the ground state (μ_g) and the lowest energy dipole allowed state (μ_i)), oscillator strength (ϕ), polarizability (α), hyperpolarizability (β), percentage of chirality (β_{xyz}), and the optical gap (δE) (the energy difference between the ground state and the lowest energy dipole allowed state) were calculated for the molecules of spacer length from $n = 1$ to $n = 12$. The corresponding values obtained by the dynamic SOS and correction vector method are shown in the tables 1 and 2.

For the twin donor-acceptor system, the even chains have very little dipole moment ($\approx 3 D$) while the odd ones have much higher dipole moment ($\approx 12 D$). The dipole moment for the single $D-A$ molecule, is calculated as, $\mu_g \approx 7.3 D$. For a perfect parallel arrangement of the dipoles, the classical non-interacting picture predicts the total dipole moment as twice the single $D-A$ molecule value for parallel arrangement and 0 for a perfect anti-parallel arrangement. While, for the even spacers the dipole moments are nearer to zero, the odd-spacers show much smaller values from the classical result of twice the single

Table 1. The ground state dipole moment, transition dipole moment, the change in dipole moment, polarizability, hyperpolarizability, percentage of chirality and EFISH β .

System	μ_g (D)	μ_t (D)	$\Delta\mu$ (D)	α (10^{-24} esu)	β (10^{-32} esu)	β_{xyz} (10^{-32} esu)	$\frac{\mu\beta}{10^{-32}}$ (esu)
CD1	12.0158	3.1567	8.8591	18.6263	76.7197	0.1153	903.2722
CD2	3.4912	4.5454	1.0542	18.1112	3.2928	0.1587	6.2674
CD3	12.3109	3.3943	8.9166	17.7776	89.1017	0.1587	1065.3001
CD4	3.4869	4.5681	1.0812	17.8422	2.5068	0.1614	4.6629
CD5	12.3344	3.4397	8.8947	17.7882	94.1268	0.1743	1134.6722
CD6	3.4786	4.5910	1.1124	18.2114	2.3422	0.1504	6.8692
CD7	12.3432	3.4481	8.8951	18.4991	95.8396	0.1370	1136.1731
CD8	3.5174	4.0483	0.5309	18.5704	14.3541	0.2035	28.1434
CD9	12.3144	3.4141	8.9003	18.6107	98.1683	0.2441	1142.6082
CD10	3.5232	3.3031	0.2201	18.5829	16.1086	0.2427	30.5099
CD11	12.3075	3.3809	8.9266	18.6232	99.0828	0.2560	1149.1025
CD12	3.5231	3.3072	0.2159	18.6409	17.7050	0.2221	33.0583
DA	7.30133	3.2115	4.0898	16.0207	16.5492	0.4866	33.5304

Table 2. Oscillator strength (f), the optical gap (δE) and the distance between the dipoles (d).

System	f	δE (eV)	d (Å)
CD1	0.2547	6.729	2.3608
CD2	0.5194	6.6185	3.7316
CD3	0.2911	6.6532	4.9649
CD4	0.5249	6.6220	6.2635
CD5	0.2979	6.6281	7.5336
CD6	0.5301	6.6215	8.8141
CD7	0.2988	6.6175	10.1048
CD8	0.4111	6.6050	11.3934
CD9	0.2928	6.6144	12.6663
CD10	0.2739	6.6096	13.9620
CD11	0.2871	6.6123	15.2297
CD12	0.2746	6.6104	16.5282
DA	0.2749	7.0173	6.4843

$D-A$ system value. Such a trend can be easily understood: for the even chains, the dipoles are staggered and almost perfectly anti-parallel, however, 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 principle axis (Datta and Pati 2005b). The even chains have very little change in dipole moment ($\Delta\mu \approx 1 D$) while the odd ones have much higher change in dipole moment ($\Delta\mu \approx 8 D$). The change in dipole moment for the single $D-A$ molecule, is calculated as, $\Delta\mu \approx 4 D$. Hence for the twin donor–acceptor system a strong odd even effect was observed in the case of dipole moments and change in dipole moments.

To understand the linear and nonlinear optical properties, the polarizability α and first frequency dependent hyperpolarizability β was calculated with varying chain lengths for the $D-A-A-D$ systems. The electronic polarizability is defined as the ratio of the induced dipole moment of a system to the applied electric field that produces the dipole moment. For systems where the electric

field induced polarization is not constrained only to the direction of applied field, polarizability is a tensor of rank 2. Kleinman's symmetry relations allows us to simplify the calculations of the tumbling average of the polarizability from the tensors as follows (Pal *et al* 2008).

$$\alpha = \frac{1}{3}(\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}). \quad (3)$$

In the case of the twin donor–acceptor system the polarizability (α) value was constant in all the odd-even series ($\approx 18 \times 10^{-24}$), while the single donor acceptor system possesses a polarizability value slightly lesser than the twin donor–acceptor system. No odd-even effects were observed on the polarizability parameters of the twin donor–acceptor systems.

The microscopic first hyperpolarizability, β is a 3rd rank tensor, which has 27 tensor components. But in the general case of a molecule with no symmetry, these 27 elements are reduced to 10 according to Kleinman symmetry for second harmonic generation $\beta(2\omega; \omega, \omega)$. Due to independent interchange of Cartesian coordinates, $\beta_{ijk} = \beta_{ikj}$. These irreducible 10 tensor components are $\beta_{xxx}, \beta_{xxy}, \beta_{xyy}, \beta_{yyy}, \beta_{xxz}, \beta_{xyz}, \beta_{yyz}, \beta_{xzz}, \beta_{yzz}$ and β_{zzz} . By taking the tensor product of these 10 tensor components, orientationally averaged hyperpolarizabilities can be calculated from the equations given below (Ouder *et al* 1977; Ouder and Chemla 1982; Bishop 1998; Pati *et al* 1999, 2001; Pal *et al* 2008).

$$\beta_{\text{vec}}(-2\omega; \omega, \omega) = \sqrt{\beta_X^2 + \beta_Y^2 + \beta_Z^2} \quad (4)$$

where

$$\beta_i = \sum_{j=x,y,z} \frac{\beta_{ijj} + \beta_{jij} + \beta_{jji}}{3}; \quad i = x, y, z. \quad (5)$$

In an electric dipole approximation, the tensor component β_{xyz} , is the chiral component of the medium and all other

nine tensor components are achiral. Because of the property of symmetric tensor product basis set elements, the value of β_{xyz} becomes zero in the tensor product. But the chiral component β_{xyz} becomes non-zero and contributes a major portion to the macroscopic (3D) second order polarizability tensor. Thus, while designing the molecule with high β value, the β_{xyz} component becomes important in macroscopic perception. The molecules which are more symmetric (less chiral) will have small values of the chiral component β_{xyz} (Ouder and Zyss 1982)

The hyperpolarizability factor shows similar trends as the dipole moment for $D-A-(CH_2)_n-A-D$ system from $n = 1$ to $n = 12$. Odd numbered $-CH_2-$ systems had high hyperpolarizability value ($76-100 \times 10^{-32}$ esu) and even numbered $-CH_2-$ systems possess low hyperpolarizability ($2-17 \times 10^{-32}$ esu). The $D-A$ system with aliphatic groups is also having $D-(CH)_5-A$, an odd number spacer, it possesses a low value of β (16.5×10^{-32} esu) compared to the other odd numbered species. But it possesses a higher value than the even numbered species. The EFISH β values also show strong odd-even oscillation phenomena.

Ouder and Chemla (1977) established a link between β and the details of a low-lying charge-transfer transition through the two-level model. NLO properties of organic charge transfer complexes like $D-\pi-A$ can be captured very nicely by this model (Bishop 1998; Pati *et al* 2001). This model assumes that the electronic properties of the molecules are determined by the ground state and a low energy charge transfer excited state. Polarization results primarily from the mixing of charge transfer state with the ground state through the interaction of the molecule with the electric field. The sum over states (SOS) formalism lies within the limit of two level model, when the contribution from higher excited states are negligible compared to the first excited state (Kanis *et al* 1994). From the two-level model, using electric dipole approximation, the second harmonic generation response (SHG) can be written as (Pati *et al* 2001)

$$\beta_{\text{two-level}} = \frac{3e^2}{2\hbar} \frac{\omega_{12} f \Delta\mu}{(\omega_{12}^2 - \omega^2)(\omega_{12}^2 - 4\omega^2)}, \quad (6)$$

where ω_{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 2, 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 2 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 (Dewar *et al* 1985; Datta and Pati 2004, 2005a, b, 2006).

The oscillator strength is a dimensionless quantity to express the relative strength of the electronic transitions within atomic and molecular systems. The oscillator strength shows remarkable features in which f -increases for even numbered spacers and decreases for odd numbered spacers. A uniform increase is observed in even numbered spacers and decrease is observed in odd numbered spacers up to the spacer length of $n = 8$. But after the spacer $n = 8$ the odd-even oscillations were not that pronounced compared to the spacer less than eight. This indicates that the spacer above $n = 8$ had little influence on the electronic transitions. Hence, it was found that the charge transfer is predominant only up to spacer = 7. The optical gap is calculated as the energy difference between the geometry relaxed ground state and the lowest optically allowed state with substantial oscillator strength (Simpson 2004). The optical gap of the systems were very high in a range of 6–7 eV. A high optical gap was observed in the $D-A$ system which prevented any coupling between donor and acceptor groups and resulted in the reduction of polarization effects.

The distance between the dipoles increases as the number of alkyl units increases. The distance between the dipoles also exhibit an influence on the odd-even phenomena. 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 (Datta and Pati 2005b, 2006). For each even spacer distance, β is smaller and for each odd spacer distance β is larger.

5. Conclusions

Semiempirical calculations were performed to understand the NLO efficiency of donor-acceptor systems with saturated spacers ($n = 1$ to $n = 12$) and the odd-even oscillation was observed. The NLO responses of the chromophores are mainly due to the electrostatic interaction on the strengths of the donor (D) and acceptor (A). For the saturated bridged molecules, electrons are localized at the respective sites and thus the electron transfer has a much shorter range. Hence the hyperpolarizability of saturated $D-A$ systems were low compared to the conjugated NLO chromophores. The single $D-A$ system behaves

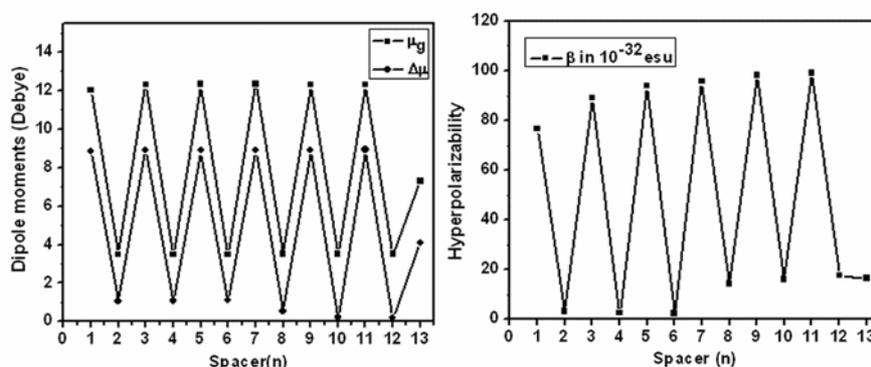


Figure 2. Pictorial representation of odd–even effects observed in ground state dipole moment (μ_g in debye), the change in dipole moment ($\Delta\mu$ in debye) and hyperpolarizability (β in 10^{-32} esu).

independent of each other, and there was no possibility for intermixing between the chromophores. It was observed that while the linear polarizability remained almost constant throughout the series, the ground state dipole moment, change in dipole moment, EFISH β and the first hyperpolarizability (β) showed strong odd–even oscillations. The hyperpolarizability value (β) showed an order of magnitude increase for odd spacers compared to the even spacers. The significantly higher SHG efficiencies for the twin *D–A* systems of odd series implies that there is a less effective cancellation of dipoles associated with the chromophores of the odd dimers compared to the even ones. In the even cases, the all trans arrangement of the alkyl spacer of the twin molecule will lead to conformers that possess a centre of symmetry, while in the odd cases it could lead to structures which may possess a mirror plane. The odd and even spacer series separately show the values to be almost constant with the increase of odd $-\text{CH}_2$ spacers and even $-\text{CH}_2$ spacers. The origin for such oscillations is attributed to the similar oscillations in the ground state dipole moment, dipole moment difference between the ground state and the dipole allowed excited 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.

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References

- Albert I D L and Ramasesha S 1990 *J. Phys. Chem.* **94** 6540
 Bishop D M 1998 *Adv. Chem. Phys.* **104** 1
 Datta A and Pati S K 2004 *J. Phys. Chem.* **A108** 320
 Datta A, Pati S K, Davis D and Sreekumar K 2005 *J. Phys. Chem.* **A109** 4112
 Datta A and Pati S K 2005a *J. Molecular Structure, Theochem.* **756** 97
 Datta A and Pati S K 2005b *Chem. Eur. J.* **11** 4961
 Datta A and Pati S K 2006 *Chem. Soc. Rev.* **35** 1305
 Davis D, Sreekumar K and Pati S K 2005 *Synth. Met.* **155** 384
 Dewar M J S, Zoebisch E G, Healy E F and Stewart J J P 1985 *J. Am. Chem. Soc.* **107** 3902
 Elizabeth C V and Sreekumar K 2008 *Proceedings SAMPADA-2008*, Pune, India
 Gaussian 03 Revision B.05 Gaussian Inc. Pittsburgh P A 2003
 Gauss J 2000 *Modern methods and algorithms of quantum chemistry*, Proceedings, 2nd edn **3** 541
 Gunter P 2000 *Nonlinear Optical Effects Mater.* **72** 11
 Kanis D R, Ratner M A and Marks T J 1994 *Chem. Rev.* **94** 195
 Li Z, Yu G, Wu W, Liu Y, Ye C, Qin J and Li Z 2009 *Macromolecules* **42** 3864
 Ouder J L and Chemla D S 1977 *J. Chem. Phys.* **66** 2664
 Ouder J L and Zyss J 1982 *Phys. Rev.* **A26** 2016
 Pal S, Manna A K and Pati S K 2008 *J. Chem. Phys.* **129** 204301
 Park G, Jung W S and Ra C S 2004 *Bull. Korean Chem. Soc.* **25** 1427
 Pati S K, Marks T J and Ratner M A 2001 *J. Am. Chem. Soc.* **123** 7287
 Pati S K, Ramasesha S, Shuai Z and Bredas J L 1999 *Phys. Rev.* **B59** 14827
 Ramasesha S and Albert I D L 1990 *Phys. Rev.* **B42** 8587
 Ramasesha S, Shuai Z and Bredas J L 1995 *Chem. Phys. Lett.* **245** 224
 Robert W and Boyd J 2009 *Biomed. Opt.* **14** 29902
 Simpson G J 2004 *Chem. Phys. Chem.* **5** 1301
 Yongjun L, Ying L, Xianghe K, Min X and Chengbu L 2000 *Theoret. Exp. Chem.* **36** 333