

A theoretical study of second hyperpolarizabilities for donor–acceptor–donor molecules

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The linear polarizabilities α and second hyperpolarizabilities γ of molecules with donor–acceptor–donor (D–A–D) motifs were calculated by a semi-empirical molecular orbital method through the finite-field approach. The bond-length alternation (BLA) parameter was used to consider the structure–property relationship for this class of molecule. By tuning the molecular ground-state geometries with the applied electric field, the dependence of the longitudinal components, α_{xx} and γ_{xxxx} , on the BLA parameter is obtained, differing from those for push–pull chromophores. With the reduction of BLA, the value of α_{xx} increases monotonously, while γ_{xxxx} is firstly positive and increases, reaches a maximum, then decreases and crosses through zero, ultimately approaching a negative maximum. The extension of the conjugation paths connecting the acceptor and the two donors leads to a rapid increase in α_{xx} and γ_{xxxx} values for short oligomers, accompanied by a sign reversion (from positive to negative) in γ_{xxxx} for some oligomers with highly polarized structures. A strategy for designing and synthesizing D–A–D-like molecules with large positive or negative third-order optical non-linearities is suggested based on the calculated results.

1. Introduction

Non-linear optical (NLO) properties of organic molecules have been extensively studied because of their potential applications in electronic and optical devices.^{1,2} Most studies for obtaining large NLO responses have focused on push–pull systems in which the electron donor (D) and electron acceptor (A) groups are connected through a π -conjugation path. A general structure–property relationship for these D–A systems has been well understood although some further modifications and improvements are still ongoing.^{3,4} It has been shown theoretically and experimentally that an enhanced NLO response can be achieved by optimizing the strength of the donor–acceptor pair and/or the nature of the conjugation path.^{5–8} Moreover, Marder and co-workers⁹ studied the correlation between static (hyper)polarizabilities and ground-state geometries in terms of the bond length alternation (BLA) parameter, defined as the difference between the average length of adjacent carbon–carbon bonds in a polymethine chain. The linear polarizabilities α , first hyperpolarizabilities β and second hyperpolarizabilities γ of D–A chromophores are sensitive to the molecular ground-state structures.

In contrast to the detailed studies on D–A systems, the structure–property relationship for donor–acceptor–donor (D–A–D) systems has so far not been systematically addressed, although some of them exhibit significant NLO activities. Some centrosymmetric squaraines with a typical D–A–D structure in which the central electron-deficient four-membered ring acts as an acceptor and the two substituents act as the donors possess unusually large negative second hyperpolarizabilities.^{10,11} Another class of D–A–D compounds, bis(styryl)benzene derivatives with electron-accepting groups attached to the central rings, were recently suggested as candidates for two-photon absorption materials.¹² Searching for new NLO materials among organometallic compounds is an active field where compounds with D–A–D structural motifs are common.^{13–15} Hence it is worthwhile investigating the NLO properties of D–A–D compounds with respect to their molecular and electronic structures.

It has been shown that theoretical calculations can play an important role in understanding the origin of the molecular NLO properties and the establishment of the relationship between molecular structures and their NLO activities.^{16,17} In this work, we performed semi-empirical molecular orbital calculations on the second hyperpolarizabilities of a D–A–D-like prototype molecule (Fig. 1, top) in which two terminal donors, amines and one central acceptor, carbonyl, are connected *via* polyene bridges. As mentioned above, most interests have focused on the third-order NLO properties of D–A–D-like molecules, most of which possess inversion symmetry and their first hyperpolarizabilities vanish. Chen *et al.*¹⁸ have already reported the first hyperpolarizabilities of some asymmetric D–A–D-like dyes. Here we restricted our studies to the static electronic second hyperpolarizabilities, as well as the linear polarizabilities of the prototypical molecule at various ground-state geometries.

In the investigation of structure dependence on the polarizabilities of D–A chromophores, two approaches are often used to control the molecular ground-state polarization and electronic configurations, in addition to adopting a large number of real donor–acceptor pairs. One is to evaluate NLO responses in simulated solvent environments with various

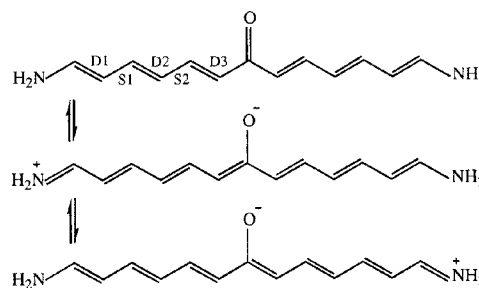


Fig. 1 Prototypical molecule with donor–acceptor–donor motif. Top, neutral resonance form; middle, one charge-transfered resonance form; bottom, the other charge-transfered resonance form.

relative permittivities.¹⁹ Experiments have clearly demonstrated that the medium influences to a large extent the molecular geometry, and as a direct consequence the NLO properties.^{20–22} Another approach is to polarize a molecule by applying an external electric field.^{23–26} The molecular equilibrium geometry and electronic configuration vary with the field strength. For D–A chromophores, the preferred method is to use a uniform electric field in the longitudinal direction since the field strength is easily controlled.^{23,26} However, this method is often unsuitable for D–A–D-like molecules, since the external electric field exerts opposite effects on the two parts partitioned at the central acceptor group. In this study, we used point-charge fields instead of a uniform field. The field strength is controlled by the distance between the point charges (also named “sparkles”) and the molecule. This method, which was implemented with the MOPAC package, is adequate to reproduce qualitatively the experimental trends in geometry and polarizabilities as a function of increasing ground-state polarization, as pointed out by Gorman and Marder.²⁴ The main advantage of this approach relative to adopting real donor–acceptor pairs is to allow us to drive the structure all the way from the neutral polyene form to the charge-separated form and thus to obtain a complete picture of the evolution.^{24,25}

The methodology is outlined in section 2. In section 3, the geometry variations of the prototypical molecule caused by the external field are discussed, as well as the linear polarizabilities and second hyperpolarizabilities for various geometries. Finally, the dependencies of α and γ on the chain length are given.

2. Computational methodology

The geometries with or without the incorporation of sparkles are optimized by using the AM1 parameterization²⁷ with the “precise” option included in the MOPAC package.²⁸ A finite field (FF) approach²⁹ with the AM1 parameterization and MNDO Hamiltonian³⁰ is used to evaluate the static linear polarizabilities α and second hyperpolarizabilities γ for every AM1-optimized molecular geometry. Both algorithms based on the energy expansion and dipole expansion are available in MOPAC, but only the results obtained from the energy-expansion method are used for the discussion below because they have a much greater numerical stability than those from the dipole-expansion method.³¹ The SCF convergence is set to 10^{-12} in the finite field procedure. The total energy E under the influence of a static electric field F is expanded as³²

$$E = E^{(0)} - \mu_i^{(0)} F_i - \frac{1}{2!} \alpha_{ij} F_i F_j - \frac{1}{3!} \beta_{ijk} F_i F_j F_k - \frac{1}{4!} \gamma_{ijkl} F_i F_j F_k F_l - \dots \quad (1)$$

where $E^{(0)}$ is the total energy in the absence of the applied field, and $\mu_i^{(0)}$, α_{ij} , β_{ijk} and γ_{ijkl} represent the permanent dipole moment, polarizability, first hyperpolarizability and second hyperpolarizability, respectively. The quantities concerned in this paper are defined in terms of the above equation.

The molecule lies in the xy plane with the polyene chain parallel to the x -axis. Two negative point charges step towards each nitrogen atom in opposite direction perpendicular to the plane, while two positive point charges step towards the oxygen in the same way (Fig. 2). The distance r between the sparkles and the nitrogen or oxygen atoms varies synchronously from 20.00 to 4.00 Å. The increase in electric-field strength with the decrease in r becomes larger, since the field strength of the point charges is inversely proportional to the square of the distance. The sparkles have little effect on the molecular structures at long distance, corresponding to the case affected by a weak external electric field. At short dis-

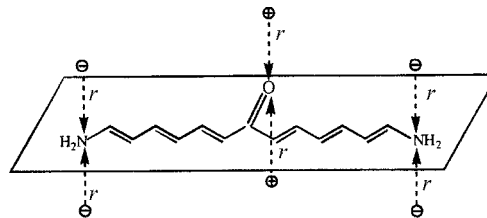


Fig. 2 External point charges (“sparkles”) approach the nitrogen and oxygen atoms in a direction perpendicular to the plane of the molecule. r is the distance between the sparkles and the targets.

tance, the influence of the sparkles significantly increases, and a small change in r may lead to a marked change in the molecular structure and properties. Therefore, different step increments are set according to the different distances. The step increment is large at long distance, and becomes smaller as the sparkles approach the molecule. For each value of r , the geometry is optimized and then the NLO susceptibilities are calculated in the presence of these point charges. For some concerned values, we used a much smaller increment of 0.01 Å in order to obtain a clear description of the structure–property relationships.

3. Results and discussion

3.1. Molecular geometry

The left and right moieties of the carbon chain shown in Fig. 1 (top) are similar both in length and structure; therefore, only half of the bond lengths are discussed. The geometry without a sparkle, *i.e.*, the free molecule, has similar structural parameters to those with sparkles placed at a long distance. As the sparkles approach the plane in which the molecule lies, they exert a considerable influence on the molecular geometry. The closer the distance r is, the stronger the influence. With the decrease of sparkle distance r from 20.0 to 4.0 Å, the original double bonds D1, D2 and D3 become longer, while the original single bonds C–N, S1, S2 and C–C(O) become shorter. The BLA parameter is defined as the average bond length difference between the three double bonds and the two single bonds.⁹ As a result, the BLA value changes from -0.083 to -0.019 Å, indicating an obvious bond length alternation variation caused by the approaching sparkles. Fig. 3 shows the evolution of the BLA value as a function of sparkle distance r . BLA is a useful parameter to describe the structural features when establishing structure–property relationships for D–A chromophores linked by polyene bridges.^{6,9,24,26} Here we found that the BLA parameter can also be used to consider the ground-state geometries of D–A–D molecules.

In π -conjugated organic systems, the molecular geometry and electronic structure are strongly related. In addition to the changes of bond length alternation, “sparkles” significantly enhance the $D^+A^-D^+$ ground-state charge separa-

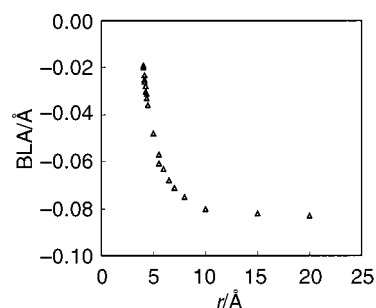


Fig. 3 Evolution of the BLA parameter with the sparkle distance r . BLA is defined as $BLA = (D1 + D2 + D3)/3 - (S1 + S2)/2$, when D1, D2, D3, S1 and S2 denote the bond lengths shown in Fig. 1.

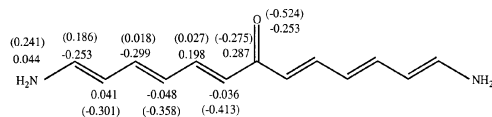


Fig. 4 AM1 calculated net charge distributions for the molecule without and with (in parentheses) the incorporation of sparkles at $r = 4.00$ Å. In either case, the left branch has an identical net charge distribution with the right. The values at the amino group are of the summation of net charges at the nitrogen and the two hydrogen atoms. All values are in atomic units.

tion at short distances. In the case without any sparkles, as shown in Fig. 4, both the amino (including N and two H atoms) and the carbonyl (including C and O atoms) groups are positively charged to a small extent, *viz.*, 0.044 and 0.034 $|e|$, respectively. When the sparkles are placed at $r = 4.00$ Å, the amino groups are still positively charged but to a larger extent, *viz.*, 0.241 $|e|$, whereas the carbonyl group becomes highly negative, $-0.249 |e|$. By comparison, each amino group loses 0.197 $|e|$ of negative charge and the carbonyl group obtains 0.283 $|e|$, indicating a distinctive charge transfer from the two terminal amino groups to the central carbonyl group caused by the incorporation of sparkles. One may note that the amount of charge received at the carbonyl group is not equal to the summation of the reduction at the two amino groups, 0.394 $|e|$. This demonstrates that the total net charge of the polyene bridges between donor and acceptor is also a structural parameter relating to the molecular ground-state geometry. In our previous studies,³³ we established a relationship between this parameter, which was denoted as the bridge atomic charge sum (BACS), and molecular NLO properties for push-pull chromophores.

The ground-state structure of a D–A chromophore can be viewed as a combination of one neutral and one charge-transferred resonance form, differing in the extent of charge separation.^{9,34,35} Analogously, the structure of a D–A–D molecule can also be regarded as a mixture of one neutral and two charge-transferred resonance forms (Fig. 1, top, middle and bottom, respectively). For weak donors and acceptor, corresponding to the situation with a large value of r , the neutral form dominates the ground state. As a result, the molecule has a high degree of BLA and a small amount of charge separation. When the donors and acceptor become stronger, *i.e.*, small value of r , the contributions from the two charge-transferred forms to the ground state increase, while those from the neutral form decrease, resulting in a BLA reduction along with an increasing charge separation. As a result, the charge-transferred forms may dominate the ground state. Ultimately, an extreme case in which the ground state is fully controlled by the two charge-transferred resonance forms may be reached. In every case, the contributions of the two charge-transferred forms are equal as long as the two donors and the two bridges are identical.

One can note that the D–A–D molecules have to some extent a similar relationship to the D–A molecules as regards their BLA parameters and charge-transferred characters. However, there is a significant difference. For a D–A molecule, the two resonance forms have opposite effects on the BLA parameter, resulting in a negative BLA value at the neutral limit, a positive BLA value at the zwitterionic limit, and zero BLA at the cyanine limit at which the original double and single bonds become identical in averaged length.^{9,34} For a D–A–D molecule, the three resonance forms have different effects on the BLA parameter. The neutral form gives a negative BLA for both branches of the molecule separated from the central carbonyl group, while one of the charge-transferred forms gives a positive BLA for the left branch and a negative BLA for the right branch, and the other form gives a negative BLA for the left branch and a positive BLA for the

right branch. As a result, the two charge-transferred forms have opposite effects on the BLA parameter. The ground-state geometry is cyanine-like, *i.e.* BLA = 0, at the most polarized limit that consists of the two charge-transferred forms without any contribution from the neutral form. Therefore, the ground state of a D–A–D molecule changes from a neutral limit to a cyanine limit while the BLA parameter ranges from negative values to zero. Correspondingly, the ground state of a D–A molecule changes from a neutral limit to a cyanine limit, then to a zwitterionic limit while the BLA parameter ranges from negative to zero, then to positive values. The BLA parameter for a D–A–D molecule ranges within half the region of that for a D–A molecule.

3.2. Linear polarizabilities and second hyperpolarizabilities

Since the prototypical molecule has a linear shape stretched along the x -axis, the molecular averaged polarizabilities are mainly dominated by the longitudinal diagonal tensor components.³⁶ For example, for the free molecule, α_{xx} (5.46×10^2 au) and γ_{xxxx} (4.42×10^5 au) (au = atomic units) contribute the major part of the isotropic averaged values of $\langle\alpha\rangle$ (2.30×10^2 au) and $\langle\gamma\rangle$ (9.28×10^5 au), which are defined as $\langle\alpha\rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ and $\langle\gamma\rangle = (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} + 2\gamma_{zzxx})/5$. Hence only the longitudinal components, α_{xx} and γ_{xxxx} , are discussed below. Fig. 5 shows the evolution of α_{xx} and γ_{xxxx} *vs.* BLA values, reflecting the relationship between the NLO properties and the ground-state geometries. Both the AM1/FF and MNDO/FF methods give a similar trend for α_{xx} and γ_{xxxx} as a function of BLA, with AM1 giving a slightly lower value of α_{xx} than MNDO when compared at the same AM1-optimized geometry.

The linear polarizability α_{xx} increases with the BLA reduction, indicating that strong donors and acceptors lead to large linear polarizabilities for D–A–D compounds. This is markedly different from that for the push-pull polyene for which α_{xx} increases and peaks at a cyanine limit and then decreases with increasing charge separation resulting from strong donors and acceptors.^{34,35}

The second hyperpolarizability γ_{xxxx} is positive and has a maximum value at BLA ≈ -0.06 Å, corresponding to the case with weak donors and acceptor. It becomes negative and may possess a significant value when BLA approaches zero, corresponding to the situation with strong donors and acceptor. Intermediately, the molecule exhibits poor third-order NLO activities in the situation where BLA is around -0.03 Å.

Compared with the behavior of the second hyperpolarizability *vs.* the BLA parameters for D–A molecules, the D–A–D molecules exhibit a different structure-property relationship. For a D–A molecule,^{9,34,35} γ_{xxxx} is firstly positive and increases, peaks, decreases, peaks in a negative sense, then again increases, peaks and decreases while its ground state changes from a neutral limit to a cyanine limit, then to a zwitterionic limit, whereas γ_{xxxx} for a D–A–D molecule covers only half the evolution from a neutral limit to a cyanine limit.

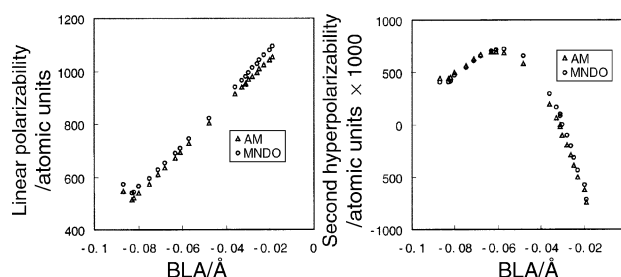


Fig. 5 AM1 and MNDO calculated linear polarizabilities and second hyperpolarizabilities as a function of BLA.

Moreover, it is found that γ_{xxxx} values for a D–A molecule are dependent on the values of α_{xx} and β_{xxx} , for example, γ_{xxxx} equals zero at a BLA value where β_{xxx} peaks, and peaks negatively at a BLA value where α_{xx} peaks.²³ These correlations were not observed for a D–A–D molecule in our study. As previously mentioned, α_{xx} of the prototypical molecule varies monotonously and β_{xxx} vanishes.

As can be seen in Fig. 5, there is an optimal BLA value that maximizes γ positively or negatively. One may obtain large positive third-order NLO polarizabilities for D–A–D compounds with given polyene bridges by optimizing the donor and acceptor of weak strength. One may also obtain large negative third-order NLO polarizabilities by employing strong substituents. Certainly, a compound with a molecular ground-state structure far from the BLA value associated with the peaks should be avoided in designing organic third-order NLO materials.

Recently, Hahn *et al.*³⁷ presented theoretical descriptions of α and γ of a linear quadrupolar molecule based on a three-state model analysis. Our results, to some extent, agree with some of their conclusions. The curves we presented for α_{xx} and γ_{xxxx} vs. BLA (Fig. 5) are similar in shape to their curves of α_{xx} and γ_{xxxx} vs. another parameter, named the charge transfer character, which is linearly proportional to the BLA parameter in the range from -0.12 to 0 Å. In addition, they calculated the longitudinal γ_{xxxx} of *p*-bisnitrobenzene derivatives and concluded that their γ_{xxxx} values were positive and increased with the replacement of strong donors. Dirk *et al.*³⁸ and other authors^{10,11} measured and calculated the γ values of squarylium dyes, showing that these D–A–D compounds possess negatively significant γ values, which increase with stronger substituents. From the above discussion, it is not surprising to find that the second hyperpolarizabilities of D–A–D compounds possess reverse sign, even reverse evolution with varying substituents, since each case can exist depending on the molecular ground-state geometries that are determined by both the strengths of the donors and acceptors and the nature of the conjugated bridges.

3.3. Chain-length dependences

We also calculated the linear polarizabilities and second hyperpolarizabilities of the prototypical molecule with various numbers N of double bonds in both branches. The results without and with sparkles at 5.50, 5.00, 4.50, 4.20 Å are listed in Table 1. For the free molecule, γ_{xxxx} is always positive and grows rapidly with extension of the π -conjugated paths up to $N = 10$, whereas α_{xx} exhibits a relatively moderate increase. Only positive values of γ_{xxxx} are obtained for the case with sparkles placed at $r = 5.50$ Å up to $N = 7$, and both α_{xx} and γ_{xxxx} show similar trends to those of the free molecule when the chain lengthens. However, for the molecule with sparkles at closer distances, $r = 5.00$, 4.50 and 4.20 Å, the sign of γ_{xxxx}

is positive for short chains, and reverses for long chains. For $r = 5.00$ Å, γ_{xxxx} is positive for $N = 1$ –4 and negative for $N = 5$ –6. For $r = 4.50$ Å, γ_{xxxx} is positive for $N = 1$ –3 and negative for $N = 4$ –6. For $r = 4.20$ Å, γ_{xxxx} is positive for $N = 1$ –2 and negative for $N = 3$ –5. As the repeat number of double bonds in both branches increases, the value of γ_{xxxx} firstly grows rapidly in the positive sense, then reverses its sign at a certain chain length and grows rapidly in the negative sense. The sign reversion occurs at a shorter chain length for a molecule with closer sparkles, indicating that the large conjugation system in a D–A–D molecule may lead to a negative value of γ_{xxxx} , particularly for those with strong donor and acceptor groups. This can be rationalized qualitatively by using the reduced three-level model^{38,39}

$$\gamma = \gamma_c + \gamma_n + \gamma_{tp} \quad (2)$$

where $\gamma_c = -K\mu_{01}^4 D_{11}$, $\gamma_n = K\mu_{01}^2 (\Delta\mu_{01})^2 D_{111}$, $\gamma_{tp} = K\mu_{01}^2 \mu_{12}^2 D_{121}$; μ_{01} is the transition moment from the ground state to the significant one-photon state, μ_{12} is the transition moment between the one-photon and the significant two-photon state, $\Delta\mu_{01}$ is the dipole moment difference between the ground and one-photon states, K is a constant defined by the optical process and D is a dispersion term. For the x -direction of the prototypical molecule, $(\Delta\mu_{01})_x = 0$, leading to a reduced model:

$$\gamma_{xxxx} = (\gamma_c)_{xxxx} + (\gamma_{tp})_{xxxx} \quad (3)$$

Thus, γ_{xxxx} depends on the competition between the two right-hand terms which are opposite in sign. Strong donor and acceptor groups tend to stabilize the one-photon state,^{34,35,38} resulting in a larger μ_{01} than μ_{12} , and as a consequence γ_c contributes mainly to γ_{xxxx} . The π -electron delocalization across bonds tends to give a smaller value of γ_{tp} ,^{35,38} so that γ_c becomes the dominant term for a molecule with a large conjugation system, leading to a negative value of γ_{xxxx} . Thus, the extension of the conjugated path in a D–A–D molecule not only results in a rapid increase in magnitude but also a sign reversion when the donors and acceptor are strong enough. Our results are in agreement with Marder's statement²⁴ that negative non-linearities could be obtained in a polar molecule by increasing the electron delocalization. The linear polarizability α_{xx} always increases with an extending chain whether the sparkles exist or not.

In a polarizability calculation in MOPAC systems, the molecule must be orientated along its principal moments of inertia before the calculation starts.⁴⁰ For polymers or molecules with long chains, an orientation problem often hampers the finite-field calculations, possibly caused by additional sparkles. Hence, we only listed in Table 1 the results for molecules with close sparkles up to 7, 6 or 5.

Generally, polarizabilities for polymers can be related exponentially to conjugation length (number of repeat units) in the form $\alpha_{xx} \propto N^m$ and $\gamma_{xxxx} \propto N^n$.⁴¹ The power laws have so far

Table 1 Linear polarizabilities and second hyperpolarizabilities of the prototypical molecule with different numbers of double bonds^a

N^b	None		$r = 5.50$		$r = 5.00$		$r = 4.50$		$r = 4.20$	
	α_{xx}/N	γ_{xxxx}/N	α_{xx}/N	γ_{xxxx}/N	α_{xx}/N	γ_{xxxx}/N	α_{xx}/N	γ_{xxxx}/N	α_{xx}/N	γ_{xxxx}/N
1	1.44	0.10	1.44	0.11	1.48	0.12	1.52	0.12	1.55	0.11
2	1.63	0.55	1.80	0.64	1.90	0.61	2.05	0.49	2.17	0.34
3	1.82	1.47	2.42	2.29	2.68	1.94	3.04	0.65	3.51	−2.47
4	1.97	2.72	3.26	6.50	3.80	3.67	4.54	−5.82	5.00	−15.6
5	2.09	4.07	4.31	15.8	5.38	−1.71	6.65	−51.6	7.09	−76.7
6	2.18	5.39	5.66	33.2	7.71	−62.8	9.08	−191		
7	2.26	6.61	7.35	58.3						
8	2.32	7.69								
9	2.36	8.63								
10	2.42	9.57								

^a r in Å, α_{xx} in 10^2 au and γ_{xxxx} in 10^5 au (au = atomic units). ^b The number of double bonds in both branches of the prototypical molecule.

not been established for D–A–D molecules with the exception of the prediction of $m = 2$ and $n = 4$ given by Hahn *et al.*³⁷ based on a three-state model. By using least-squares fitting, we obtained $m = 1.27$ and $n = 2.97$ for the free molecules. Certainly, the power laws are approximately valid only for shorter conjugated oligomers, since γ_{xxxx} of oligomers generally saturates with longer chains.

4. Conclusion

The linear polarizabilities and second hyperpolarizabilities of polyene-linked donor–acceptor–donor systems were calculated by the finite-field approach with the AM1 parameterization and MNDO Hamiltonian. By using point charges (sparkles) to simulate solvent effects, the strengths of the donor and acceptor along with the molecular polarization were tuned to investigate the structure–property relationship. A correlation between the BLA parameters and the ground-state structures was found in a different way with respect to the push–pull compounds. The linear polarizability increases monotonously with reduction of the BLA value. However, the second hyperpolarizability is initially positive and increases, peaks, and then drops, reverses its sign, and finally reaches a negative maximum. In addition to the donor–acceptor strengths, the nature of the conjugation paths is another factor that determines the magnitude, even sign, of the second hyperpolarizabilities. To design and synthesize compounds with large positive second hyperpolarizabilities, one should choose a weak donor and acceptor, along with a short conjugated chain. Contrarily, one can obtain compounds with large negative second hyperpolarizabilities by choosing a strong donor and acceptor, along with a long conjugated chain. This strategy based on semi-empirical MO calculations is supported by some theoretical and experimental evidence. Further systematic examination of this strategy is needed.

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