International Scholarly Research Network
ISRN Physical Chemistry
Volume 2012, Article ID 262563, 8 pages
doi:10.5402/2012/262563

Research Article

Theoretical Study of Effect of the Number of N,N-dimethyl-4-nitroaniline Units in Novel "Parallel Connection" Chromophores on Its Nonlinear Optical Properties

Chao-Zhi Zhang,[1] Hui Cao,[2] and Zhao-Bing Guo[1]

[1] *Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of Environmental Science & Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China*
[2] *Department of Theoretical Chemistry, School of Biotechnology, Royal Institute of Technology, 106 91 Stockholm, Sweden*

Correspondence should be addressed to Chao-Zhi Zhang, zhangchaozhi@nuist.edu.cn

Received 5 August 2011; Accepted 17 September 2011

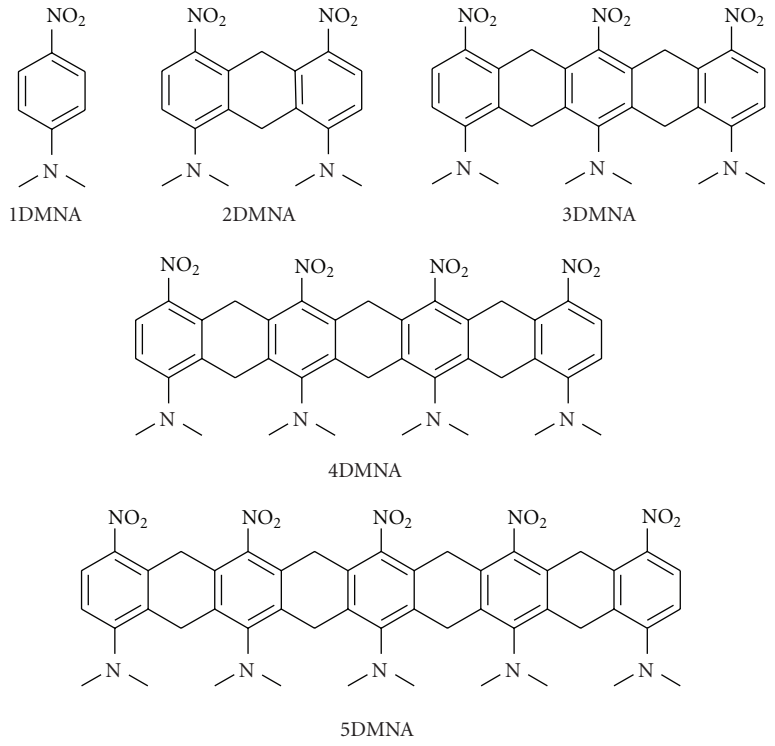
Academic Editors: T. Kar, H. Reis, and M. Sliwa

Design of "parallel connection" chromophores could give a way of acquiring effective chromophores. The semiempirical method ZINDO was employed to study relationship between static first hyperpolarizabilities of "parallel connection" chromophores and the number of parallel nonconjugated N,N-dimethyl-4-nitroaniline (DMNA) units in the chromophore. The results show that the chromophore containing three parallel non-conjugated DMNA units exhibits the highest static first hyperpolarizability, which is 1.8 times that of chromophore DMNA. However, static first hyperpolarizabilities of the chromophores containing four or five DMNA units are very small. The absorption maximum wavelength (λ_{max}) of "parallel connection" chromophores is remarkably shorter (34.9 nm–38.1 nm) than that of **1DMNA**. Therefore, the "parallel connection" chromophore containing three DMNA units would be an effective chromophore with a large first hyperpolarizability and a good optical transparency. It could give a useful suggestion for designing effective chromophores containing parallel non-conjugated D-π-A units.

1. Introduction

Organic and polymeric second-order nonlinear optical (NLO) materials have attracted much attention due to their potential applications in the fields of telecommunication, optical data storage, and optical information processing [1–8]. Chromophores always play a key role in design of effective NLO materials. The first hyperpolarizability β of a chromophore increases with increasing length of the conjugated π system and increasing strength of the donor and/or acceptor [9–13]. Generally, an increase in the β value is accompanied by a bathochromic shift due to a larger π-conjugated length and/or stronger donor and acceptor ability [9–13]. Therefore, there is always a tradeoff between nonlinearity and transparency [14–23]. To resolve this problem, we had designed and synthesized a series of H-typed chromophores with two parallel and nonconjugated D-π-A units [24–27]. The results of hyper-Rayleigh scattering (HRS) and UV-vis spectra show that the first hyperpolarizability (β) values of H-typed chromophores are remarkably increased compared with the corresponding mono-D-π-A unit reference compounds without causing a large shift of the absorption band to longer wavelength [24–27]. It suggests an available way of solving the tradeoff between nonlinearity and transparency in designing NLO chromophores, that is, design of chromophore with parallel and non-conjugated multi-D-π-A units.

Relationship between NLO properties and a π-conjugated length in a "series connection" chromophore is an interesting subject and has been investigated comprehensively in theoretical and experimental areas [9, 28–32]. Similarly, it would be very interesting that relationship between the β_0



Scheme 1: Structures of "parallel connection" chromophores containing DMNA units.

of chromophores and the number of parallel non-conjugated D-π-A units in a "parallel connection" chromophore would be investigated. N,N-dimethyl-4-nitroaniline (DMNA) is an effective chromophore and usually is used as a reference chromophore for study of NLO properties of chromophores [33, 34]. Therefore, a series of chromophores with two or multiple parallel and non-conjugated DMNA units were designed, and their static first hyperpolarizabilities (β_0) were given from quantum chemistry calculations for investigating relationship between static first hyperpolarizabilities of "parallel connection" chromophores and the number of parallel non-conjugated DMNA units in the chromophore (Scheme 1).

2. Computational Details

The structure geometries of all chromophores were optimized by the density functional theory (DFT) calculations using Gaussian03 software at the B3LYP/6-31G(d) level [35, 36]. Then, the semiempirical method ZINDO was used to calculate their first hyperpolarizabilities [37–43].

3. Results and Discussion

3.1. NLO Properties of "Parallel Connection" Chromophores. We have reported that the Semi-Empirical method ZINDO would be a suitable method for calculating the first hyperpolarizabilities of "parallel connection" chromophores when electronic acceptors are strong electron-withdrawing group NO_2 [44]. The reason could be that interactions between parallel non-conjugated D-π-A units are taken into account when the ZINDO method is used for calculating the first hyperpolarizabilities. Therefore, the semi-empirical method ZINDO was employed to study the effect of the number of DMNA units in a "parallel connection" chromophore on its NLO properties.

The NLO properties of chromophores containing two or multiple parallel and non-conjugated **DMNA** units were given based on theoretical calculations. The calculated values of these chromophores are shown in Table 1.

Table 1 shows that static first hyperpolarizability of **3DMNA** acquired from the methods ZINDO is the highest. Enhancement of β_0 value of **3DMNA** is 1.8 times as β_0 value of DMNA. Enhancement of β_0 value of **2DMNA** is 0.8 times as β_0 value of DMNA. However, static first hyperpolarizabilities of **4DMNA** and **5DMNA** are quite small due to interactions between DMNA units.

3.2. Relationship between Static First Hyperpolarizabilities of "Parallel Connection" Chromophores and the Number of Parallel Nonconjugated DMNA Units in the Chromophore. Figure 1 shows clearly that β_0 value of chromophore decreases from 24.1×10^{-30} esu to 19.0×10^{-30} esu with increasing the number of parallel and non-conjugated **DMNA** units in the chromophore from 1 to 2. Then β_0 value of the chromophore increases from 19.0×10^{-30} esu to 44.1×10^{-30} esu with increasing the number of parallel and non-conjugated **DMNA** units in the chromophore from 2 to 3. The β_0 value decreases rapidly from 44.1×10^{-30} esu to -0.1×10^{-30} esu with increasing the number of **DMNA** units in the

Table 1: Linear and nonlinear properties of the designed "parallel connection" chromophores are calculated by ZINDO.

No.	$\Delta\mu_{eg}$ (D)	μ_{eg} (D)	μ_g [a] (D)	λ_{max} [b] (nm)	$\Delta\lambda$ [c]	E_{eg} (ev)	β_0 (10^{-30} esu)	E [d]
1DMNA	6.138	6.138	8.07	369.9	0	3.352	24.1	1.0
2DMNA	6.086	6.104	11.31	331.8	38.1	3.736	19.0	0.8
3DMNA	7.871	8.100	15.77	335.0	34.9	3.701	44.1	1.8
4DMNA	−0.955	1.165	19.75	332.0	37.9	3.734	−0.1	−0.004
5DMNA	0.332	3.210	24.34	332.7	37.2	3.727	1.1	0.05

[a]Dipole moment at ground state. [b]The absorption maximum wavelength. [c]Blue shift of the absorption maximum wavelength (the values were calculated according to following method: $\Delta\lambda = \lambda_{max}$ of **1DMNA**—λ_{max} of "parallel connection" chromophores.). [d]Enhancement of β_0 of "parallel connection" chromophores compared with that of 1DMNA (the values were calculated according to following method: β_0 of chromophores containing DMNA units/β_0 of 1DMNA).

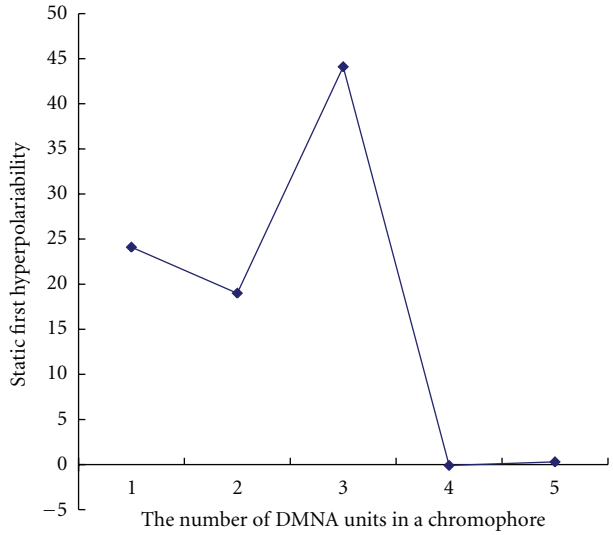


Figure 1: Relationship between static first hyperpolarizabilities of "parallel connection" chromophores and the number of **DMNA** units in the chromophore.

chromophore from 3 to 4. At last, β_0 value of the chromophore increases slightly from -0.1×10^{-30} esu to 1.1×10^{-30} esu with increasing the number of parallel and nonconjugated **DMNA** units in the chromophore from 4 to 5. It shows that β_0 value of the chromophore would decrease when the number of parallel non-conjugated DMNA units in the chromophore increases (a **DMNA** unit) from an odd to an even. However, β_0 value of the chromophore would increases when the number of parallel non-conjugated DMNA units in the chromophore increases (a **DMNA** unit) from an even to an odd.

The two-state model (1) is usually employed to estimate the first hyperpolarizability of chromophore [37–43]:

$$\beta^{\text{two-state}} = \underbrace{\frac{3\mu_{eg}^2\Delta\mu_{eg}}{E_{eg}^2}}_{\text{Static factor}} \times \underbrace{\frac{\omega_{eg}^2}{\left(1-4\omega^2/\omega_{eg}^2\right)\left(\omega_{eg}^2-\omega^2\right)}}_{\text{Dispersion factor}}, \quad (1)$$

where μ_{eg} is the transition dipole moment between the ground state $|g\rangle$ and the charge-transfer excited state $|e\rangle$, $\Delta\mu_{eg}$ is the difference in dipole moment, and E_{eg} is the transition energy. ω_{eg} is angular frequency corresponding to the transition between the ground and the first excited state; ω is the angular frequency of incident light.

According to the two-state model, β_0 values depend on the differences of energy between the ground and the first excited states (E_{eg}), the transition dipole moment between the ground state $|g\rangle$ and the charge-transfer excited state $|e\rangle$(μ_{eg}) and the difference in dipole moment ($\Delta\mu_{eg}$).

Figure 2 shows clearly that nitro group and benzene ring in **DMNA** are coplanar. Two benzene rings and their respective substituted nitro group are noncoplanar in a **2DMNA** molecule compared with the structure of 1DMNA due to steric repulsion between two dimethylamino groups and electrostatic repulsion between O25, and O28 atoms in a 2DMNA.

Generally, a HOMO energy level and a LUMO energy level depend on the electron-donating strength of donor and the electron-withdrawing strength of acceptor, respectively [45]. From the structure of 2DMNA, the probability of transition from ground to excited state in a **DMNA** unit containing atom N30 would be the biggest, because the difference between the charge of nitro group containing atoms N26, O27, and O28 and the charge of dimethylamino group containing atom N30 is the biggest. As we know, if π electrons could be delocalized well in a DMNA unit, the difference of energy levels between HOMO of amino group and LUMO of nitro group should be small, and electron distribution should be uneven and further results in a large difference between the charge of nitro group and the charge of dimethylamino group. The transition from ground to excited state would result in increasing the charge of a nitro group containing atoms N26, O27, and O28. The charge of another nitro group containing atoms N23, O24, and O25 would decrease due to electrostatic repulsion between O25 and O28 atoms when π electron is excited. The electrostatic repulsion would result in the benzene ring and their respective substituted nitro group containing atoms N23, O24, and O25 being non-coplanar in a **DMNA** unit and further reducing dipole moment of the unit at the excited state. Therefore, increase of an excited dipole moment of DMNA unit and decrease of another excited dipole of DMNA unit would slightly decrease $\Delta\mu_{eg}$ and μ_{eg} value of **2DMNA** compared with 1DMNA. According to the two-state model [37–43], the first hyperpolarizability of **2DMNA** could be smaller than that of DMNA.

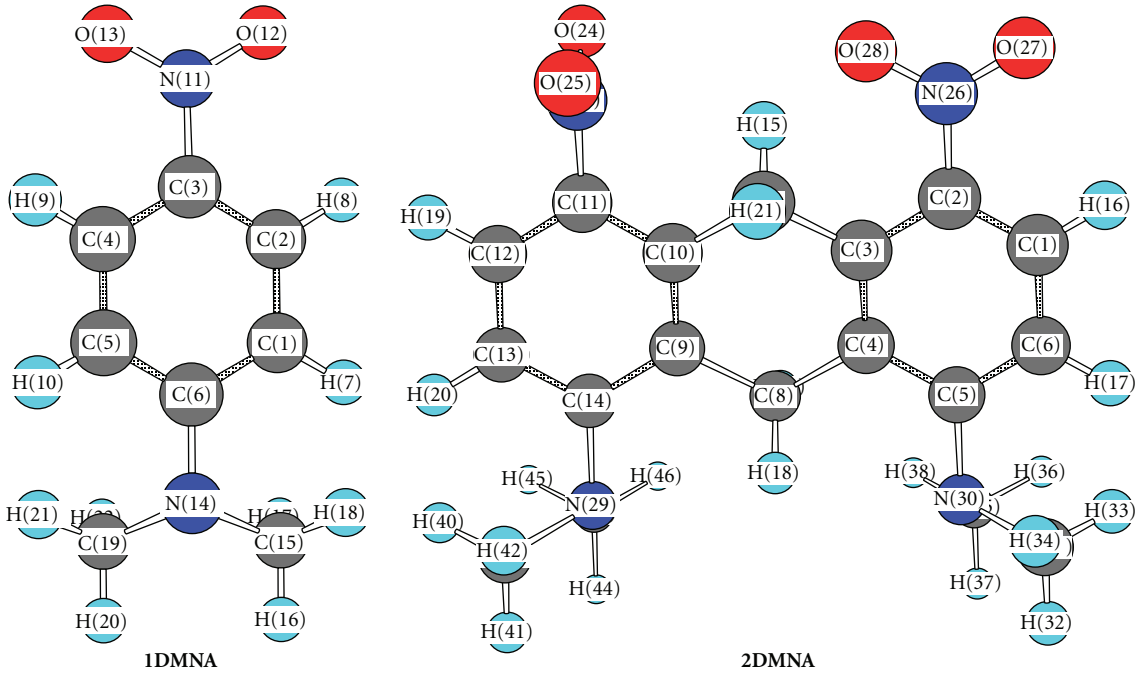


Figure 2: The structures of **1DMNA** and **2DMNA** optimized by DFT and atomic charges (unit: atomic unit) of N and O atoms (the numbers in brackets are charges of nitro and dimethylamino groups).

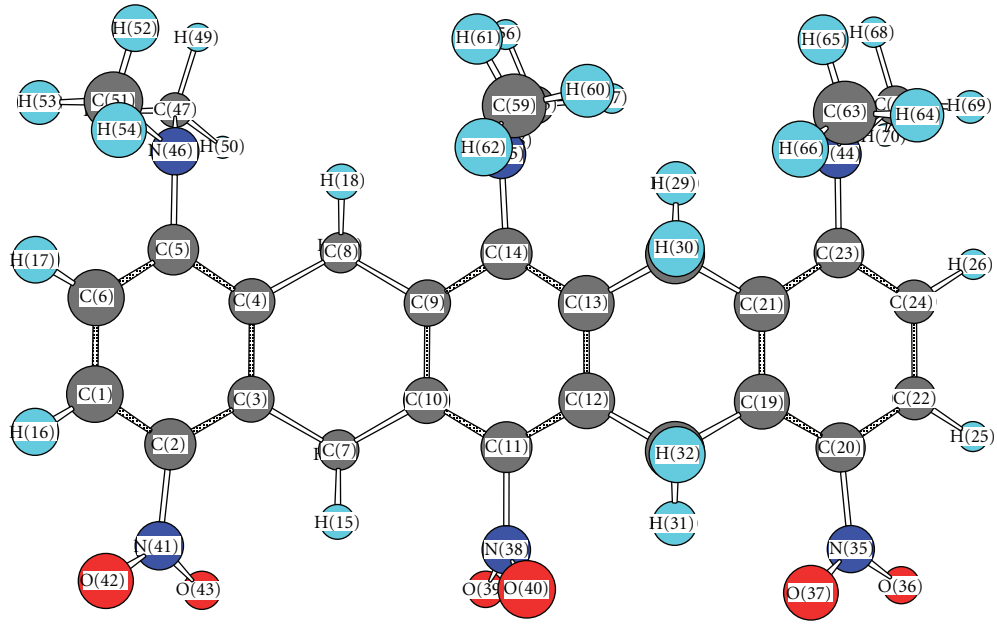


Figure 3: The structures of **3DMNA** optimized by DFT and atomic charges (unit: atomic unit) of N and O atoms (the numbers in brackets are charges of nitro and dimethylamino groups).

Similarly, Figure 3 shows clearly that three benzene rings and their respective substituted nitro groups are noncoplanar in a **3DMNA** molecule compared with the structure of 1DMNA due to steric repulsion between dimethylamino groups and electrostatic repulsion between O37 and O40 atoms and between O39 and O43 atoms in a 3DMNA.

Based on a two-state model, Di Bella et al. [46, 47] estimated that the NLO response of hypothetical **PNA** trimer would have a sharp increase, when three **PNA** molecules were arranged in the same direction and distance between two adjacent PNA molecules was shorter than 3.0 Å. In the present case, the three **DMNA** units in a single

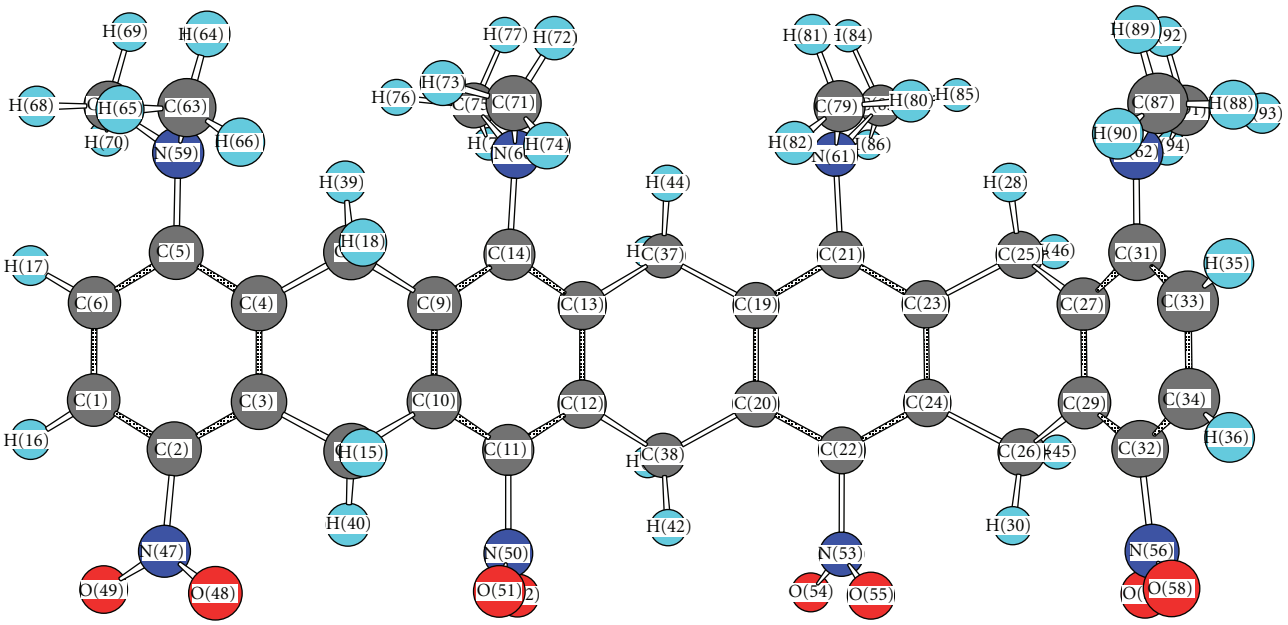


FIGURE 4: The structures of **4DMNA** optimized by DFT and atomic charges (unit: atomic unit) of N and O atoms (the numbers in brackets are charges of nitro and dimethylamino groups).

molecule are nearly arranged in the same direction and the limited distances between two adjacent **DMNA** units are 2.520 Å (C3–C10) and 2.513 Å (C12–C19), respectively from computational results of **3DMNA**. Therefore, it implies that the **3DMNA** can exhibit large second-order NLO responses because close contact among three **DMNA** units in a molecule induces the strong dipole-dipole interaction among three **DMNA** units.

From the structure of **3DMNA**, the probability of transition from ground to excited state in the **DMNA** unit containing atom N41 would be the biggest, because the difference between the charge of nitro group containing atoms N41, O42, and O43 and the charge of dimethylamino group containing atoms N46 is the biggest. The electrostatic repulsion would further result in the benzene ring and their respective substituted nitro group containing atoms N38, O39, and O40 being non-coplanar in a **DMNA** unit and further reducing dipole moment at the excited state. However, the charge of a nitro group containing atoms N35, O36, and O37 would increase due to decreasing electrostatic repulsion between O37 and O40 atoms when π electron was excited. The decreasing electrostatic repulsion would enhance coplanarity of the **DMNA** unit containing atom N35. Therefore, increases of excited dipoles of two **DMNA** units and decrease of an excited dipole of **DMNA** unit would increase of $\Delta\mu_{eg}$ and μ_{eg} values of **3DMNA**. According to the two-state model [37–43], **2DMNA**could exhibit a large the first hyperpolarizability.

Similarly, Figure 4 shows clearly that four benzene rings and their respective substituted nitro groups are non-coplanar in a **4DMNA** molecule due to steric repulsion between dimethylamino groups and electrostatic repulsion between two adjacent O atoms, such as O57 and O55, O54 and O52, and O51 and O48 atoms.

From the structure of **4DMNA**, the probability of transition from ground to excited state in the DMNA unit containing atom N56 would be the biggest. Similarly, increases of excited dipole moments of two **DMNA** units and decreases of excited dipole moments of two **DMNA** units would decrease μ_{eg} and $\Delta\mu_{eg}$ values of **4DMNA**. According to two-state model, the first hyperpolarizability of **4DMNA** would be smaller than that of **1DMNA.** Moreover, the first hyperpolarizability values of **4DMNA** would depend on interactions among **DMNA** units in a chromophore. Here the local field corrections due to interactions among DMNA units begin to play an important role in determining the first molecular hyperpolarizability [48–50]. The interactions among four **DMNA** units in **4DMNA** could result in a small $\Delta\mu_{eg}$ and μ_{eg} value of **4DMNA**.

Similarly, Figure 5 shows clearly that five benzene rings and their respective substituted nitro groups are non-coplanar in a **5DMNA** molecule due to steric repulsion between dimethylamino groups and electrostatic repulsion between two adjacent O atoms, such as O61 and O63, O64 and O67, O66 and O70, and O69 and O73 atoms.

From the structure of **5DMNA**, the probability of transition from ground to excited state in the DMNA unit containing atom N71 would be the biggest. Similarly, increases of excited dipole moments of three **DMNA** units and decreases of excited dipole moments of two **DMNA** units would induce a small β_0 value of **5DMNA**. Moreover, the first hyperpolarizability values of **5DMNA** would depend on interactions among DMNA units in a chromophore. Here the local field corrections due to interactions among DMNA units begin to play an important role in determining the first molecular hyperpolarizability [48–50]. The interactions among five **DMNA** units in **5DMNA** could result in a small $\Delta\mu_{eg}$ and μ_{eg} value of **5DMNA**.

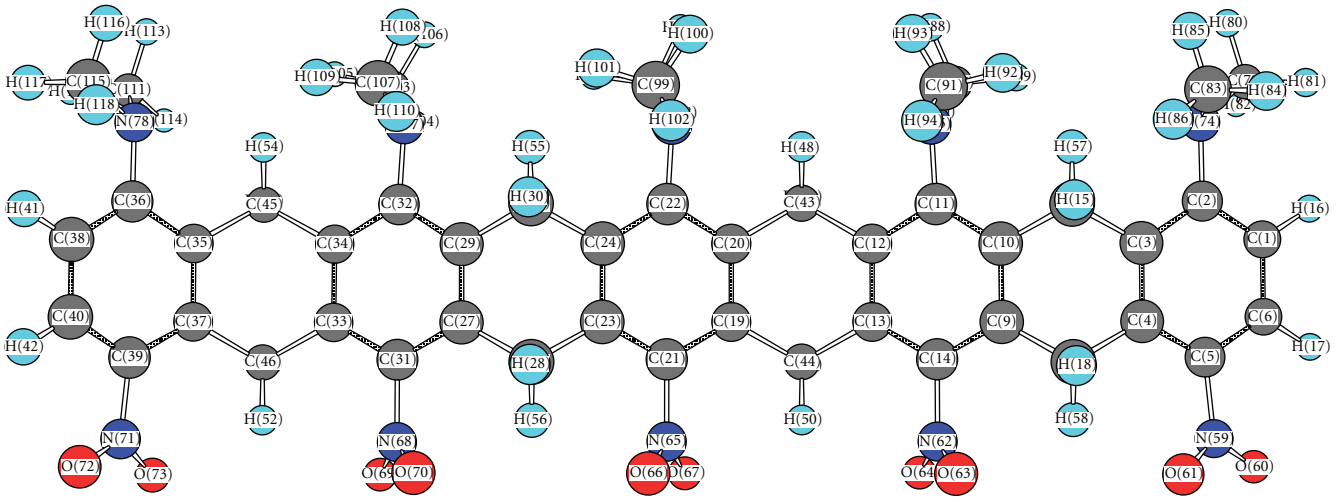


FIGURE 5: The structures of **5DMNA** optimized by DFT and atomic charges (unit: atomic unit) of N and O atoms (the numbers in brackets are charges of nitro and dimethylamino groups).

3.3. Optical Transparency of "Parallel Connection" Chromophores. Table 1 shows clearly that the absorption maximum wavelength (λ_{max}) of "parallel connection" chromophores is remarkably shorter than that of **1DMNA**. Blue shift of the absorption maximum wavelength of "parallel connection" chromophores is at the range from 34.9 nm to 38.1 nm compared with **1DMNA**. The main reason is that π electrons would be better delocalized in the **1DMNA** than those in "parallel connection" chromophores containing two or multi-DMNA units, because nitro group and benzene ring in **1DMNA** are coplanar and benzene rings and their respective substituted nitro group are non-coplanar in the "parallel connection" chromophores due to steric repulsion between dimethylamino groups and electrostatic repulsion between two adjacent O atoms. Therefore, the "parallel connection" chromophores containing two or multi DMNA units have shorter λ_{max} than **1DMNA**. It implies that these "parallel connection" chromophores would exhibit good optical transparency. It suggests that design of chromophores containing three parallel non-conjugated **DMNA** units would be an effective strategy for designing NLO chromophores with a large β_0 value and good optical transparency.

4. Conclusion

The structure geometries of five chromophores were optimized by the density functional theory (DFT) calculations using Gaussian03 software at the B3LYP/6-31G(d) level. Then, the Semi-Empirical method ZINDO was employed to study relationship between static first hyperpolarizabilities of "parallel connection" chromophores and the number of parallel non-conjugated N,N-dimethyl-4-nitroaniline (DMNA) units in the chromophore. The results show that the chromophore containing three parallel non-conjugated DMNA units exhibits the highest static first hyperpolarizability, which is 1.8 times that of chromophore **1DMNA**. However, static first hyperpolarizabilities of the chromophores containing four or five **DMNA** units are very small. The β_0 value of the chromophore would decrease when the number of parallel non-conjugated DMNA units in the chromophore increases (a **DMNA** unit) from an odd to an even. However, β_0 value of the chromophore would increase when the number of parallel non-conjugated DMNA units in the chromophore increases (a **DMNA** unit) from an even to an odd. The absorption maximum wavelength (λ_{max}) of "parallel connection" chromophores is remarkably shorter (34.9 nm–38.1 nm) than that of **1DMNA**. It implies that these "parallel connection" chromophores would exhibit good optical transparency. Therefore, the "parallel connection" chromophore containing three **DMNA** units would be an effective chromophore with a large first hyperpolarizability and a good optical transparency. It could give a useful suggestion for designing effective chromophores containing parallel non-conjugated D-π-A units.

Acknowledgment

This work was supported by the grant fund of Nanjing University of Information Science & Technology for C. Z. Zhang.

References

[1] S. R. Marder, B. Kippelen, A. K. Y. Jen, and N. Peyghambarian, "Design and synthesis of chromophores and polymers for electro-optic and photorefractive applications," *Nature*, vol. 388, no. 6645, pp. 845–851, 1997.

[2] A. Qin, F. Bai, and C. Ye, "Design of novel X-type second-order nonlinear optical chromophores with low ground state dipole moments and large first hyperpolarizabilities," *Journal of Molecular Structure*, vol. 631, pp. 79–85, 2003.

[3] Y. Shi, C. Zhang, H. Zhang et al., "Low (sub-1-volt) halfwave voltage polymeric electro-optic modulators achieved by controlling chromophore shape," *Science*, vol. 288, no. 5463, pp. 119–122, 2000.

[4] C. Ruslim and K. Ichimura, "Conformation-assisted amplification of chirality transfer of chiral Z-azobenzenes," *Advanced Materials*, vol. 13, no. 1, pp. 37–40, 2001.

[5] M. Asghari-Khiavi, P. Hojati-Talemi, and F. Safinejad, "Polarizability and first-order hyperpolarizability of cyclic imides," *Journal of Molecular Structure*, vol. 910, no. 1–3, pp. 56–60, 2009.

[6] Y.-X. Sun, Q.-L. Hao, W.-X. Wei et al., "Experimental and density functional studies on 4-(3,4-dihydroxybenzylideneamino)antipyrine, and 4-(2,3,4-trihydroxybenzylideneamino) antipyrine," *Journal of Molecular Structure*, vol. 904, no. 1–3, pp. 74–82, 2009.

[7] M. Medveď, S. Budzák, D. Jacquemin, and E. A. Perpète, "Enhancement of the second-order NLO responses of boron-nitrogen oligomers by copolymerization with polyyne," *Journal of Molecular Structure*, vol. 901, no. 1–3, pp. 194–201, 2009.

[8] F. Ibersiene, D. Hammoutène, A. Boucekkine, C. Katan, and M. Blanchard-Desce, "DFT study of NLO properties of boroxine based octupolar molecules," *Journal of Molecular Structure*, vol. 866, no. 1–3, pp. 58–62, 2008.

[9] T. Verbiest, S. Van Elshocht, M. Kauranen et al., "Strong enhancement of nonlinear optical properties through supramolecular chirality," *Science*, vol. 282, no. 5390, pp. 913–915, 1998.

[10] V. Alain, L. Thouin, M. Blanchard-Desce et al., "Molecular engineering of push–pull phenylpolyenes for nonlinear optics: improved solubility, stability, and nonlinearities," *Advanced Materials*, vol. 11, no. 14, pp. 1210–1214, 1999.

[11] E. Norambuena, C. Olea-Azar, A. Delgadillo, M. Barrera, and B. Loeb, "Comparative evaluation of the acceptor properties of quinone derivatized polypyridinic ligands," *Chemical Physics*, vol. 359, no. 1–3, pp. 92–100, 2009.

[12] Y. J. Cheng, J. Luo, S. Huang et al., "Donor-acceptor thiolated polyenic chromophores exhibiting large optical nonlinearity and excellent photostability," *Chemistry of Materials*, vol. 20, no. 15, pp. 5047–5054, 2008.

[13] P. K. Nandi, K. Mandal, and T. Kar, "Theoretical study of static second-order nonlinear optical properties of push-pull heteroquinonoid dimers," *Journal of Molecular Structure*, vol. 760, no. 1–3, pp. 235–244, 2006.

[14] C. Ye, "Nonlinear optical materials," in *Organic Solids*, F. Wang and D. Zhu, Eds., chapter 5, p. 188, Shanghai Science Press, Shanghai, China, 1999.

[15] T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays, and A. Persoons, "Second-order nonlinear optical materials: recent advances in chromophore design," *Journal of Materials Chemistry*, vol. 7, no. 11, pp. 2175–2189, 1997.

[16] L. T. Cheng, W. Tam, S. R. Marder, A. E. Stiegman, G. Rikken, and C. W. Spangler, "Experimental investigations of organic molecular nonlinear optical polarizabilities. 2. A study of conjugation dependences," *Journal of Physical Chemistry*, vol. 95, no. 26, pp. 10643–10652, 1991.

[17] L. T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, and S. R. Marder, "Experimental investigations of organic molecular nonlinear optical polarizabilities. 1. Methods and results on benzene and stilbene derivatives," *Journal of Physical Chemistry*, vol. 95, no. 26, pp. 10631–10643, 1991.

[18] Y. Pan and X. Tang, "Synthesis and properties of novel Y-shaped nonlinear optical polymers containing imidazole-based chromophores," *Journal of Applied Polymer Science*, vol. 108, no. 5, pp. 2802–2807, 2008.

[19] J. Zyss, I. Ledoux, S. Volkov et al., "Through-space charge transfer and nonlinear optical properties of substituted paracyclophane," *Journal of the American Chemical Society*, vol. 122, no. 48, pp. 11956–11962, 2000.

[20] A. Carella, A. Castaldo, R. Centore, A. Fort, A. Sirigu, and A. Tuzi, "Synthesis and second order nonlinear optical properties of new chromophores containing 1,3,4-oxadiazole and thiophene rings," *Journal of the Chemical Society, Perkin Transactions 2*, no. 11, pp. 1791–1795, 2002.

[21] J. A. Hansen, J. Becher, J. O. Jeppesen et al., "Synthesis and non-linear optical properties of mono-pyrrolotetrathiafulvalene derived donor-π-acceptor dyads," *Journal of Materials Chemistry*, vol. 14, no. 2, pp. 179–184, 2004.

[22] A. Facchetti, A. Abbotto, L. Beverina et al., "Azinium-(π-bridge)-pyrrole NLO-phores: influence of heterocycle acceptors on chromophoric and self-assembled thin-film properties," *Chemistry of Materials*, vol. 14, no. 12, pp. 4996–5005, 2002.

[23] B. Zhao, W.-Q. Lu, Z.-H. Zhou, and Y. Wu, "The important role of the bromo group in improving the properties of organic nonlinear optical materials," *Journal of Materials Chemistry*, vol. 10, no. 7, pp. 1513–1517, 2000.

[24] C.-Z. Zhang, C. Lu, J. Zhu et al., "The second-order nonlinear optical materials with combined nonconjugated D-π,-A units," *Chemistry of Materials*, vol. 18, no. 26, pp. 6091–6093, 2006.

[25] C. -Z. Zhang, C. Lu, J. Zhu et al., "Enhanced nonlinear optical activity of molecules containing two D-π-A chromophores locked parallel to each other," *Chemistry of Materials*, vol. 20, no. 14, pp. 4628–4641, 2008.

[26] C. Z. Zhang, J. Zhu, H. Yang, C. Lu, G. Y. Lu, and Y. Cui, "Azo dyes of hexafluoroisopropylidene derivatives: synthesis and nonlinear optical properties," *Dyes and Pigments*, vol. 76, no. 3, pp. 765–774, 2008.

[27] C. Z. Zhang, J. Zhu, C. Lu, G. Y. Lu, and Y. Cui, "Relationship between optical nonlinearities of H-shaped chromophores and electronegativities of their substituent groups," *Materials Chemistry and Physics*, vol. 114, no. 2-3, pp. 515–517, 2009.

[28] R. K. David, A. R. Mark, and J. M. Tobin, "Design and construction of molecular assemblies with large second-order optical nonlinearities. Quantum chemical aspects," *Chemical Reviews*, vol. 94, no. 1, pp. 195–242, 1994.

[29] P. C. Ray, P. Bonifassi, and J. Leszczynski, "Effect of conjugation path length on quadratic nonlinear optical properties of monomer and aggregates of zwitterionic merocyanine dyes," *Journal of Physical Chemistry A*, vol. 110, no. 28, pp. 8963–8969, 2006.

[30] A. Datta and S. Pal, "Effects of conjugation length and donor-acceptor functionalization on the non-linear optical properties of organic push-pull molecules using density functional theory," *Journal of Molecular Structure*, vol. 715, no. 1–3, pp. 59–64, 2005.

[31] S. Keinan, M. J. Therien, D. N. Beratan, and W. Yang, "Molecular design of porphyrin-based nonlinear optical materials," *Journal of Physical Chemistry A*, vol. 112, no. 47, pp. 12203–12207, 2008.

[32] H. Li, K. Han, X. Shen et al., "The first hyperpolarizabilities of hemicyanine cationic derivatives studied by finite-field (FF) calculations," *Journal of Molecular Structure*, vol. 767, no. 1–3, pp. 113–118, 2006.

[33] O. Y. Borbulevych, R. D. Clark, A. Romero et al., "Experimental and theoretical study of the structure of N,N-dimethyl-4-nitroaniline derivatives as model compounds for non-linear optical organic materials," *Journal of Molecular Structure*, vol. 604, no. 1, pp. 73–86, 2002.

[34] B. Zhao, Z.-H. Zhou, and X.-L. Tan, "The roles of the non-centrosymmetrically substituted groups in several aromatic NLO materials," *Gaodeng Xuexiao Huaxue Xuebao*, vol. 22, p. 1728, 2001.

[35] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., Gaussian 03, Revision B.04, Gaussian, Inc., Pittsburgh, Pa, USA, 2003.

[36] S. P. Karna and M. J. Dupuis, "Frequency dependent nonlinear optical properties of molecules: formulation and implementation in the HONDO program," *Journal of Computational Chemistry*, vol. 12, no. 4, pp. 487–504, 1991.

[37] F. Li, Q. Zheng, G. Yang, and P. Lu, "Molecular structure and visible absorption maximum of cobalt phthalocyanine: quantum calculations via semi-empirical methods," *Dyes and Pigments*, vol. 77, no. 2, pp. 277–280, 2008.

[38] A. Karakas, H. Unver, and A. Elmali, "The investigation of electronic properties and microscopic second-order nonlinear optical behavior of 1-salicylidene-3-thio-semicarbazone," *Journal of Nonlinear Optical Physics and Materials*, vol. 16, no. 1, pp. 91–99, 2007.

[39] P. C. Ray, P. K. Das, and S. J. Ramasesha, "A comparative study of first hyperpolarizabilities of the acidic and basic forms of weak organic acids in water," *Journal of Chemical Physics*, vol. 105, no. 21, pp. 9633–9639, 1996.

[40] S. Houbrechts, K. Clays, A. Persoons, Z. Pikramenou, and J. M. Lehn, "Hyper-Rayleigh scattering investigation of nitrobenzyl pyridine model compounds for optical modulation of the hyperpolarisability," *Chemical Physics Letters*, vol. 258, no. 3-4, pp. 485–489, 1996.

[41] E. Hendrickx, K. Clays, and A. Persoons, "Hyper-Rayleigh scattering in isotropic solution," *Accounts of Chemical Research*, vol. 31, no. 10, pp. 675–683, 1998.

[42] G. J. T. Heesink, A. G. T. Ruiter, N. F. Van Hulst, and B. Bölger, "Determination of hyperpolarizability tensor components by depolarized hyper Rayleigh scattering," *Physical Review Letters*, vol. 71, no. 7, pp. 999–1002, 1993.

[43] S. Ramasesha, Z. Shuai, and J. L. Brédas, "Correction vector method for exact dynamic NLO coefficients in restricted configuration space," *Chemical Physics Letters*, vol. 245, no. 2-3, pp. 224–229, 1995.

[44] C. Z. Zhang, H. Cao, C. Im, and G. Y. Lu, "Theoretical study of nonlinear optical properties of "parallel connection" chromophores containing parallel nonconjugated D-π-A units," *Journal of Physical Chemistry A*, vol. 113, no. 44, pp. 12295–12303, 2009.

[45] N. Leclerc, A. Michaud, K. Sirois, J. F. Morin, and M. Leclerc, "Synthesis of 2,7-carbazolenevinylene-based copolymers and characterization of their photovoltaic properties," *Advanced Functional Materials*, vol. 16, no. 13, pp. 1694–1704, 2006.

[46] D. Di Bella, M. A. Ratner, and T. J. Marks, "Design of chromophoric molecular assemblies with large second-order optical nonlinearities. A theoretical analysis of the role of intermolecular interactions," *Journal of the American Chemical Society*, vol. 114, no. 14, pp. 5842–5849, 1992.

[47] S. Di Bella, I. L. Fragalá, M. A. Ratner, and T. J. Marks, "Electron donor-acceptor complexes as potential high-efficiency second-order nonlinear optical materials. A computational investigation," *Journal of the American Chemical Society*, vol. 115, no. 2, pp. 682–686, 1993.

[48] J. Zyss and D. S. Chemla, "Quadratic nonlinear optics and optimization of second-order nonlinear response of organic molecules and crystals," in *Nonlinear Optical Properties of Organic Molecules and Crystals*, D. S. Chemla and J. Zyss, Eds., vol. 1, p. 23, Academic Press, New York, NY, USA, 1987.

[49] M. Hurst and R. W. Munn, "Theory of molecular opto-electronics. I -Macroscopic and microscopic response. II - Environmental effects on molecular response," *Journal of Molecular Electronics*, vol. 2, pp. 35–41, 1986.

[50] R. W. Munn, "Structure of N,N-Dimethyl-4-nitroaniline," *Physics Bulletin*, vol. 39, p. 202, 1988.