

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/222626133>

Third-order nonlinear optical properties of open-shell singlet molecular aggregates composed of diphenalenyl diradicals

ARTICLE *in* SYNTHETIC METALS · NOVEMBER 2009

Impact Factor: 2.25 · DOI: 10.1016/j.synthmet.2009.07.035

CITATIONS

2

READS

31

6 AUTHORS, INCLUDING:

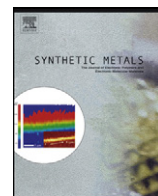


Masayoshi Nakano

Osaka University

337 PUBLICATIONS 4,781 CITATIONS

SEE PROFILE



Third-order nonlinear optical properties of open-shell singlet molecular aggregates composed of diphenalenyl diradicals

M. Nakano*, H. Fukui, H. Nagai, T. Minami, R. Kishi, H. Takahashi

Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka, Osaka 560-8531, Japan

ARTICLE INFO

Article history:

Received 16 July 2008

Received in revised form 16 July 2009

Accepted 22 July 2009

Available online 18 August 2009

Keywords:

Nonlinear optics
Hyperpolarizability
Open-shell system
Spin multiplicity
Radical

ABSTRACT

The longitudinal static second hyperpolarizabilities (γ) of one-dimensional open-shell singlet diphenalenyl radical clusters (up to trimer) are investigated using the spin-unrestricted hybrid density functional theory, UBHandHLYP, method. The longitudinal γ values per monomer for these clusters are found to significantly increase with increasing the number of monomers: the increase ratio [$\gamma/n(n-1)/\gamma(\text{monomer})$] is 2.0 (dimer) and 3.1 (trimer). The significant enhancement is predicted to be caused by the field-induced intermolecular virtual charge transfer between the both-end-phenalenyl rings, originating in the strong covalent interaction between the unpaired electrons of the cofacial phenalenyl rings.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Recently, we have theoretically proposed a novel class of third-order nonlinear optical (NLO) systems based on open-shell molecules [1–8]. In particular, singlet open-shell molecules, e.g., singlet diradicals, are found to exhibit a significant dependence of γ values – the microscopic origin of the third-order NLO properties – on the diradical character [2–8]: the γ value increases with increasing diradical character, attains the maximum, and then decreases in the large diradical character region. This behavior suggests that stable singlet diradical molecules with intermediate diradical character could be promising candidates for highly efficient third-order NLO substances as compared to conventional closed-shell NLO molecules [3,6–9]. Recently, Kamada et al. have measured two-photon absorption (TPA), which is one of typical third-order NLO phenomena, on *s*-indaceno[1,2,3-*cd*;5,6,7-*c'd'*]diphenalene (IDPL) and dicyclopenta[*b*;g]naphthaleno[1,2,3-*cd*;6,7,8-*c'd'*]diphenalene (NDPL), and have found that these exhibit the largest TPA cross-sections in pure hydrocarbon molecules [10]. As a real aggregate systems composed of diradical molecules, Kubo et al. have reported that a one-dimensional (1D) slipped stacked chain of IDPLs exhibits an unusually short π – π distance, large conductivity as well as an absorption peak shifted extraordinarily to the low-energy region [11]. The effects of crystal packing have been investigated for closed-shell systems and particularly for model polyacetylene

chains and other carbon species [12–23]. These studies have clarified a strong impact of packing on the γ , enhancing it or reducing it as a function of the relative position of the interacting units. In contrast, such crystal packing effects on the third-order NLO properties have not been sufficiently elucidated for diradicals. Using the spin-unrestricted hybrid density functional theory (DFT) method, we have recently elucidated the intermolecular interaction effects on the enhancement of γ of IDPL by considering a slipped stacked cofacial dimer, which originates in the strong covalent interaction between the unpaired electrons of the cofacial phenalenyl rings. In this study, we further investigate the trimer composed of IDPLs with a slipped stacked 1D chain arrangement in order to clarify the size dependences of γ per IDPL monomer as well as of average diradical character and of spin density distributions.

2. Model systems and calculation methods

Fig. 1 displays the structure of monomer IDPL [7] (a) and of its slipped stacked dimer (b). In IDPL, which belongs to D_{2h} symmetry, the longitudinal axis (z) is defined to be parallel to the main inertial axis. The structure of dimer with the average π – π distance of 3.137 Å (experimental value) is constructed from that of monomer optimized by the spin-unrestricted (U) B3LYP/6-31G** method [7]. The γ value using this structure is found to be in good agreement with that using the geometry determined by the X-ray diffraction data [11]. These geometrical data are employed for the trimer. We evaluate the diradical character using the spin-unrestricted Hartree–Fock (UHF) calculations. The diradical character y_i , related to the HOMO- i and LUMO+ i , is defined by the weight of the doubly-

* Corresponding author. Tel.: +81 6 6850 6265; fax: +81 6 6850 6268.
E-mail address: mnaka@cheng.es.osaka-u.ac.jp (M. Nakano).

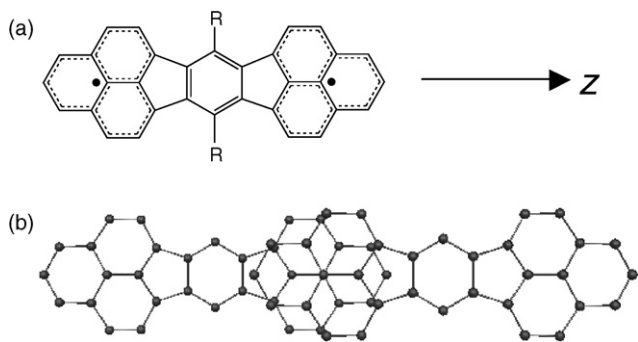


Fig. 1. Structures of IDPL monomer (a) and dimer (top view) (b).

excited configuration in the multi-configurational (MC)-SCF theory and is formally expressed in case of the spin-projected UHF (PUHF) theory as [24,25]:

$$y_i = 1 - \frac{2T_i}{1 + T_i^2}, \quad (1)$$

where T_i is the orbital overlap between the corresponding orbital pairs [24,25] and can also be represented by using the occupation numbers (n_i) of UHF natural orbitals (UNOs):

$$T_i = \frac{n_{\text{HOMO}-i} - n_{\text{LUMO}+i}}{2}. \quad (2)$$

The PUHF diradical character takes a value between 0 and 1, which represent closed-shell and pure diradical states, respectively. For the n -mer, we consider n pairs of HOMO- i and LUMO+ i ($i=0, 1, \dots, n-1$), which define the diradical characters y_i , respectively. The average diradical character (y_{av}) is defined by the arithmetic average of these diradical characters.

We apply the finite-filed approach using the (U)BHandHLYP/6-31G* method [26] to the calculation of the longitudinal γ (γ_{zzzz}) values of IDPL systems based on our previous results [1–3]. All calculations are performed using the Gaussian 03 program package [26]. In order to elucidate the intermolecular interaction-induced effects on γ , we analyze the γ density, $\rho^{(3)}(r)$, determined by the third-order numerical differentiation of the electron density $\rho(r)$ with respect to the applied field [27]. The positive and negative values of $\rho^{(3)}(r)$ multiplied by F_z^2 represent, respectively, the field-induced increases and decreases in the charge density in proportion to F_z^3 . The intermolecular interaction effect on γ can be illuminated by examining the differences of $\rho^{(3)}(r)$ between the interacting [$\rho_{\text{int}}^{(3)}(r)$] and non-interacting [$\rho_{\text{non-int}}^{(3)}(r)$] systems:

$$\rho_{\text{diff}}^{(3)}(r) = \rho_{\text{int}}^{(3)}(r) - \rho_{\text{non-int}}^{(3)}(r). \quad (3)$$

3. Results and discussion

Table 1 lists the diradical characters (y_0 , y_1 and y_2) and their average y_{av} as well as γ/n (n : the number of monomers) for the monomer, dimer and trimer. The increase in diradical character y_i is observed with increasing the number of monomers: $y_0 = 0.770$ (monomer) < 0.898 (dimer) < 0.949 (trimer), and $y_1 = 0.508$ (dimer) < 0.600 (trimer), while the relation $y_{i+1} < y_i$ holds for each n -mer ($0 \leq i \leq n-2$), e.g., y_2 (0.461) < y_1 (0.600) < y_0

Table 1
Diradical characters (y_0 , y_1 , y_2 and y_{av}) and γ_{zzzz}/n values of IDPL clusters.

	y_0	y_1	y_2	y_{av}	γ_{zzzz}/n [$\times 10^3$ a.u.]
Monomer	0.770	–	–	0.770	2284
Dimer	0.898	0.508	–	0.703	4539
Trimer	0.949	0.600	0.461	0.670	6979

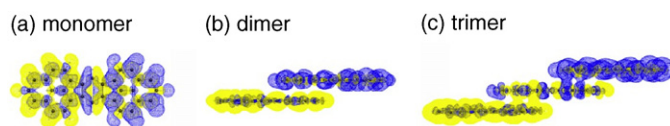


Fig. 2. γ density distribution of monomer (top view) (a) and the difference distributions of the dimer (side view) (b) and the trimer (side view) (c). The yellow and blue meshes represent positive and negative densities with iso-surface ± 500 a.u., respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

(0.949) for the trimer. As a result, the average diradical character (y_{av}) tends to decrease with increasing the number of monomers. We next examine the Mulliken spin density distributions of IDPL monomer, dimer and trimer. For all systems, the dominant α and β spin density distributions are found to be separated into right- and left-hand side phenalenyl ring regions, respectively, though spin polarizations are observed in the phenalenyl rings [7]. For the dimer, the spin density amplitude on each cofacial phenalenyl ring (0.781) is smaller than that of the monomer (0.903) whereas that of the end-phenalenyl rings (0.910) is larger. For the trimer, the spin density amplitudes on the both-end-phenalenyl rings are similarly enhanced (0.910) as compared to those on cofacial rings in the middle region [0.780 (in both-end monomers) and 0.787 (in middle monomer)].

The interaction-induced increase ratio, $R = \gamma(n\text{-mer}) / (n \times \gamma(\text{monomer}))$, is found to be 1.99 for the dimer and 3.06 for the trimer, the feature of which indicates that a substantial intermolecular interaction-induced enhancement of γ/n is still preserved for the trimer. From our previous analysis including comparison with similar-size closed-shell dimer [7], such significant increase is specific to the open-shell singlet clusters with intermediate y_{av} .

In order to reveal the origin of the interaction-induced increase of γ in the IDPL clusters, we investigate the γ density difference distribution [Eq. (3)] of the dimer and the trimer as well as γ density distribution of the monomer (see Fig. 2). As shown in our previous papers [3,7], the large $\gamma(\text{monomer})$ value is caused by the extended positive and negative π -electron γ densities well-separated, respectively, on the left- and right-hand side phenalenyl rings. For the dimer, the γ density difference distribution, which is positive on one monomer, while negative on the other monomer, indicates the field-induced virtual charge transfer (CT) between the monomers. The trimer turns out to exhibit dominant contribution to γ from field-induced virtual CT between the both-end monomers through the middle monomer having slight amplitudes of difference densities. From these results, the significant enhancement of γ/n with increasing the cluster size is predicted to originate in the strong covalent interaction between the unpaired electrons of the cofacial phenalenyl rings of the monomers with intermediate diradical characters, and not to be saturated at the size of trimer.

4. Summary

The substantial intermolecular interaction-induced enhancement of γ/n for the slipped stacked cofacial clusters of IDPLs (up to trimer) is predicted using the spin-unrestricted hybrid DFT approach. This originates in the strong covalent interaction between the unpaired electrons of the cofacial phenalenyl rings. Such features demonstrate the applicability of open-shell molecular-based aggregates to the future nano-devices in photonics. In order to confirm the tendency of size dependence of γ/n and to obtain the extrapolated γ/n value at the large size limit, we have to perform the calculations of γ for larger size aggregates, in which we will also need to employ the long-range corrected DFT approach

[28,29] in order to improve the non-local effects of exchange functional on γ [30,31]. This is in progress in our laboratory.

Acknowledgments

This work is supported by Grant-in-Aid for Scientific Research (Nos. 20655003 and 21350011) from Japan Society for the Promotion of Science (JSPS), Grant-in-Aid for Scientific Research on Priority Areas (No. 18066010) from the Ministry of Education, Science, Sports and Culture of Japan.

References

- [1] M. Nakano, et al., *J. Phys. Chem. A* 108 (2004) 4105.
- [2] M. Nakano, R. Kishi, et al., *J. Phys. Chem. A* 109 (2005) 885.
- [3] M. Nakano, T. Kubo, et al., *Chem. Phys. Lett.* 418 (2006) 142.
- [4] M. Nakano, R. Kishi, et al., *J. Phys. Chem. A* 110 (2006) 4238.
- [5] M. Nakano, R. Kishi, S. Ohta, et al., *J. Chem. Phys.* 125 (2006) 074113.
- [6] M. Nakano, R. Kishi, et al., *Phys. Rev. Lett.* 99 (2007) 033001.
- [7] M. Nakano, A. Takebe, et al., *Chem. Phys. Lett.* 454 (2008) 97.
- [8] M. Nakano, H. Nagai, *Chem. Phys. Lett.* 467 (2008) 120.
- [9] P.C. Jha, Z. Rinkevicius, H. Ågren, *J. Chem. Phys.* 130 (2009) 014103.
- [10] K. Kamada, K. Ohta, T. Kubo, et al., *Angew. Chem. Int. Ed.* 46 (2007) 3544.
- [11] T. Kubo, A. Shimizu, et al., *Angew. Chem. Int. Ed.* 44 (2005) 6564.
- [12] P.C.M. McWilliams, Z.G. Soos, *J. Chem. Phys.* 95 (1991) 2127.
- [13] B. Kirtman, in: S.P. Karna, A.T. Yeates (Eds.), *Theoretical and Computational Modeling of NLO and Electronic Materials*, American Chemical Society Series, vol. 628, American Chemical Society, New York, Washington, DC, 1996, p. 58.
- [14] S.Y. Chen, H.A. Kurtz, *J. Mol. Struct.* 388 (1996) 79.
- [15] T. Hamada, *J. Chem. Soc. Faraday Trans.* 92 (1996) 3165.
- [16] B. Champagne, B. Kirtman, *J. Chem. Phys.* 109 (1998) 6450.
- [17] O. Xie, C.W. Dirk, *J. Phys. Chem. B* 102 (1998) 9378.
- [18] B. Kirtman, C.E. Dykstra, B. Champagne, *Chem. Phys. Lett.* 305 (1999) 132.
- [19] L. Jensen, P.O. Åstrand, A. Osted, J. Kongsted, K.V. Mikkelsen, *J. Chem. Phys.* 116 (2002) 4001.
- [20] L. Jensen, K.O. Sylvester-Hvid, K.V. Mikkelsen, P.O. Åstrand, *J. Phys. Chem. A* 107 (2003) 2270.
- [21] E. Botek, B. Champagne, *Chem. Phys. Lett.* 370 (2003) 197.
- [22] M. Nakano, R. Kishi, T. Nitta, B. Champagne, E. Botek, K. Yamaguchi, *Int. J. Quantum Chem.* 102 (2005) 702.
- [23] M. Guillaume, B. Champagne, *Phys. Chem. Chem. Phys.* 7 (2005) 3284.
- [24] K. Yamaguchi, in: R. Carbo, M. Klobukowski (Eds.), *Self-consistent Field: Theory and Applications*, Elsevier, Amsterdam, 1990, p. 727.
- [25] S. Yamanaka, M. Okumura, M. Nakano, K. Yamaguchi, *J. Mol. Struct.* 310 (1994) 205.
- [26] M.J. Frisch, et al., *GAUSSIAN 03*, Revision B.04, Gaussian Inc., Pittsburgh, PA, 2003.
- [27] M. Nakano, I. Shigemoto, S. Yamada, K. Yamaguchi, *J. Chem. Phys.* 103 (1995).
- [28] H. Iikura, T. Tsuneda, T. Yanai, K. Hirao, *J. Chem. Phys.* 115 (2001) 3540.
- [29] Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, K. Hirao, *J. Chem. Phys.* 120 (2004) 8425.
- [30] B. Champagne, F.A. Bulat, W. Yang, S. Bonness, B. Kirtman, *J. Chem. Phys.* 125 (2006) 194114.
- [31] B. Kirtman, S. Bonness, A. Ramirez-Solis, B. Champagne, H. Matsumoto, H. Sekino, *J. Chem. Phys.* 128 (2008) 114108.