

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/244135632>

Second hyperpolarizabilities of polycyclic aromatic hydrocarbons involving phenalenyl radical units

ARTICLE *in* CHEMICAL PHYSICS LETTERS · JANUARY 2006

Impact Factor: 1.9 · DOI: 10.1016/j.cplett.2005.10.109

CITATIONS

89

READS

20

12 AUTHORS, INCLUDING:



Masayoshi Nakano

Osaka University

337 PUBLICATIONS 4,793 CITATIONS

SEE PROFILE



Takashi Kubo

Osaka University

136 PUBLICATIONS 2,989 CITATIONS

SEE PROFILE



Ryohei Kishi

Osaka University

110 PUBLICATIONS 1,955 CITATIONS

SEE PROFILE

Second hyperpolarizabilities of polycyclic aromatic hydrocarbons involving phenalenyl radical units

Masayoshi Nakano ^{a,*}, Takashi Kubo ^b, Kenji Kamada ^c, Koji Ohta ^c, Ryohei Kishi ^a,
Suguru Ohta ^a, Nozomi Nakagawa ^a, Hideaki Takahashi ^a, Shin-ichi Furukawa ^a,
Yasushi Morita ^b, Kazuhiro Nakasuji ^b, Kizashi Yamaguchi ^b

^a Division of Chemical Engineering, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University,
1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

^b Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

^c Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan

Received 8 October 2005; in final form 19 October 2005

Available online 16 November 2005

Abstract

The static second hyperpolarizabilities (γ) of polycyclic hydrocarbons involving phenalenyl radical units, IDPL and PDPL, are calculated by the hybrid density functional theory (DFT), BHandHLYP, method. These molecules exhibit intermediate and somewhat large diradical characters and turn out to provide about one-order larger γ values than similar size closed-shell polycyclic hydrocarbons, in which diradical character disappears. This is in agreement with our previous prediction that the diradical molecules with intermediate diradical characters tend to enhance γ values as compared to the closed-shell molecules.

© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Recently, we have found a new class of nonlinear optical (NLO) molecules, open-shell NLO molecules [1–4], based on our structure–property relations extracted from the theoretical and computational studies on the variation of second hyperpolarizability (γ), which is the microscopic origin of the third-order NLO property, of H₂ molecule during the bond dissociation [5,6]. One of these structure–property relations states that the singlet diradical molecules with intermediate and somewhat large diradical characters tend to provide significantly enhanced γ values than closed-shell molecules, which most of conventional NLO systems belong to. This can also be restated that the systems in the intermediate and somewhat strong correlation regimes, e.g., intermediate and somewhat large bond breaking regions, exhibit larger γ values than those in the

weak correlation regime, e.g., stable bond region [7,8]. Such feature is understood by the fact that the intermediate bonding electrons are sensitive to the applied field, leading to large fluctuation of electrons, i.e., large polarization. Our previous computational studies confirm the validity of this structure–property relation using *p*-quinodimethane model [2] and π -conjugated molecules involving imidazole and triazole rings [9].

In this study, we first investigate the γ values of real singlet diradical molecules involving phenalenyl units, i.e., pentaleno[1,2,3-*cd*;4,5,6-*c'd'*]diphenalene (PDPL) and s-indaceno[1,2,3-*cd*;5,6,7-*c'd'*]diphenalene (IDPL) [10], and elucidate the diradical character dependence of static γ calculated by the hybrid density functional theory (DFT) method. As a reference system, we examine a closed-shell polycyclic aromatic hydrocarbon with a similar π -conjugation size to PDPL and IDPL. From the comparison of γ among these molecules, the diradical character dependence of γ is clarified for phenalenyl systems. The spatial contributions of electrons to γ are elucidated by the γ density

* Corresponding author. Fax: +81 668506268.

E-mail address: mnaka@cheng.es.osaka-u.ac.jp (M. Nakano).

analysis [11]. From these results, we discuss a possibility of diradical NLO systems involving phenalenyl units.

2. Molecular geometries and calculation methods

Fig. 1 displays the geometrical structures of diradical molecules, PDPL (a) and IDPL (b), and a similar size closed-shell polycyclic hydrocarbon, PY2 (c), in their singlet ground states, which are optimized at the RB3LYP level of approximation using the 6-31G* basis set. For PDPL (a) and IDPL (b), both-end phenalenyl units tend to give diradicals due to the π -conjugation in the central double bond in pentalene part of PDPL and the recovery of aromaticity in the central benzene ring in s-indacene part of IDPL, respectively. On the other hand, for PY2, the closed-shell structure is expected since the Kekulé structures can be written as described by Fig. 1c. Indeed, the large bond alternations for PY2, e.g., (r_1, r_2) [Å] = (1.432, 1.366), tend to well reflect the Kekulé structures, while the bond alternations become smaller $[(r_1, r_2)$ [Å] = (1.417, 1.387) for PDPL and (1.416, 1.386) for IDPL] and thus π -electron delocalization are observed in the phenalenyl units to stabilize diradicals for PDPL and IDPL.

The diradical character, which represents a tendency of diradical nature, is calculated from 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-excited configuration in the multiconfigurational (MC)-SCF theory and is formally expressed in the case of the spin-projected UHF (PUHF) theory as [7,8]

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

where T_i is the orbital overlap between the corresponding orbital pairs [7,8] ($\chi_{\text{HOMO}-i}$ and $\eta_{\text{HOMO}-i}$) and can also be represented by using the occupation numbers (n_i) of UHF natural orbitals (UNOs):

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

Since the PUHF diradical characters amount to 0% and 100% for closed-shell and pure diradical states, respectively, y_i represents the diradical character, i.e., the instability of the chemical bond. The present calculation scheme using the UNOs is the simplest but it can well reproduce the diradical characters calculated by other methods, such as the ab initio configuration interaction (CI) method [8,12]. It is noted that the present formula employs the UHF NOs instead of UDFT NOs, which leads to incorrect lower diradical character in the present formula. Table 1 gives the diradical characters y calculated from Eqs. (1) and (2) using HOMO and LUMO of UNOs for PDPL (Fig. 1a), IDPL (Fig. 1b) and PY2 (Fig. 1c). In agreement with our speculation, it is found that the diradical characters y of PDPL and IDPL are 0.5833 and 0.7461, respectively, which represent intermediate diradical systems,

while that of PY2 is zero, which implies a closed-shell system. The fact that the y value of IDPL is larger than that of PDPL can be understood by a larger stabilization of both-end phenalenyl radicals due to the recovery of aromaticity in the central benzene ring for IDPL than PDPL.

We use the hybrid DFT, i.e., spin unrestricted (U)/restricted (R) BHandHLYP, method [13] to calculate the longitudinal γ values. Although it is well known that the use of extended basis sets are necessary for obtaining quantitative γ values for π -conjugated systems [14,15], we use the standard basis set, 6-31G*, since the size of the systems in this study prohibits the use of such large basis sets and the γ value for IDPL using the 6-31G* + diffuse p ($\zeta = 0.0523$) is shown to be slightly (10%) enhanced as compared to that using the 6-31G* at the RHF level, which suggests that the use of 6-31G* basis set is adequate for semi-quantitative comparisons of, at least, longitudinal components of γ among the large-size systems in this study. It is shown from the previous study on the p -quinodimethane models [2] that the UBHandHLYP gives reliable γ values for diradical molecules with intermediate and large diradical characters, while the RBHandHLYP method gives reliable γ values for diradical molecules with small diradical characters or closed-shell molecules, at least for molecules of the size investigated in this study. We confine our attention to the dominant longitudinal components of static γ (γ_{xxxx}) (see Fig. 1) using the finite field approach [16], which consists in the fourth-order differentiation of energy E with respect to different amplitudes of the applied external electric field. The power series expansion convention (usually called B convention) is chosen for defining γ [17]. We adopt a 4-point procedure using field amplitudes of 0.0, 0.001, 0.002, and 0.003 a.u. [11]:

$$\gamma = \{E(3F) - 12E(2F) + 39E(F) - 56E(0) + 39E(-F) - 12E(-2F) + E(-3F)\}/36(F)^4. \quad (3)$$

Here, $E(F)$ indicates the total energy in the presence of the field F applied in the longitudinal direction. This has enabled us to reach an accuracy of 10–100 a.u. on the static longitudinal γ . All calculations are performed using the GAUSSIAN 98 program package [13].

3. Second hyperpolarizability density analysis

We briefly explain the second hyperpolarizability (γ) density analysis [11], which characterizes the spatial contributions of electrons to γ . The contributions obtained from a pair of positive and negative γ densities provide a description of local contributions of electrons to the total γ . This method is based on the expression,

$$\lambda = -\frac{1}{3!} \int r \rho^{(3)}(\mathbf{r}) d^3r, \quad (4)$$

where

$$\rho^{(3)}(\mathbf{r}) = \left. \frac{\partial^3 \rho(\mathbf{r})}{\partial F \partial F \partial F} \right|_{F=0}. \quad (5)$$

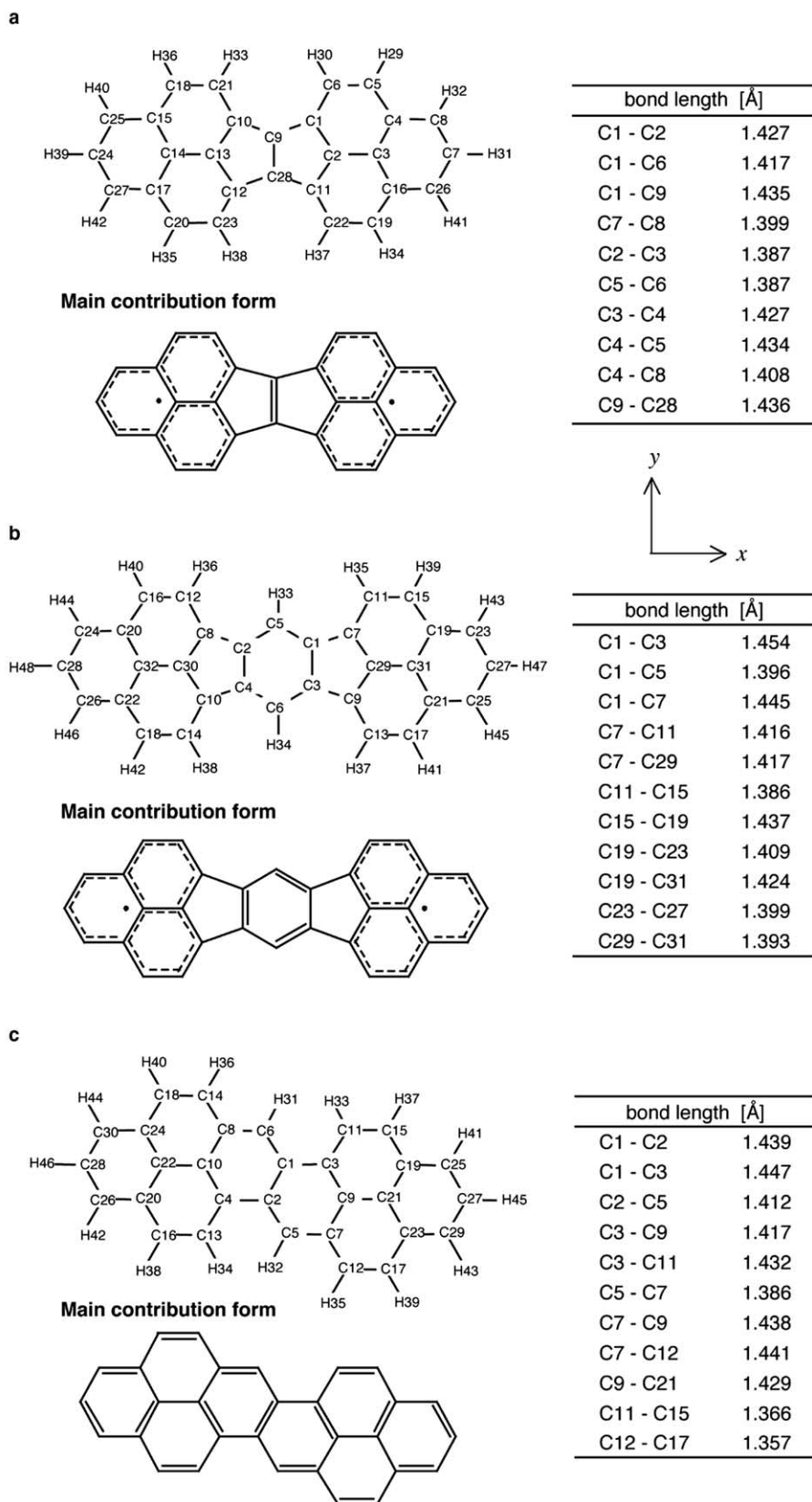


Fig. 1. Molecular geometries, main contribution forms of singlet states of PDPL (a), IDPL (b) and PY2 (c) optimized by the RB3LYP/6-31G** method. Coordinate axis and atom numbers are also shown. The corresponding structures are planar and those of PDPL and IDPL belong to D_{2h} , while PY2 does to C_{2h} point groups. The middle C1–C2 bond of PY2 has an angle of 30° with respect to the longitudinal (x) axis.

Table 1

Diradical character (γ) and second hyperpolarizability (γ_{xxxx}) of PDPL (a), IDPL (b) and PY2 (c) shown in Fig. 1

System	γ	γ ($\times 10^3$ a.u.)
(a) PDPL	0.5833	1255
(b) IDPL	0.7461	2383
(c) PY2	0	194

The γ values are given in a.u. (1.0 a.u. of second hyperpolarizability = 6.235377×10^{-65} C⁴ m⁴ J⁻³ = 5.0367×10^{-40} esu). The calculations of diradical characters are performed using the occupation numbers of UNOs and those of γ are done using the UBHandHLYP method for (a) and (b) and RBHandHLYP method for (c) with the 6-31G* basis set.

This third-order derivative of the electron density with respect to the applied electric fields, $\rho^{(3)}(\mathbf{r})$, is referred to as the γ density. It is noted that the positive and negative values of γ densities multiplied by F^3 correspond respectively to the field-induced increase and decrease in the charge density (in proportion to F^3), which induce the third-order dipole moment (third-order polarization) in the direction from positive to negative γ densities. Therefore, the γ density map represents the relative phase and magnitude of change in the third-order charge densities between two spatial points with positive and negative values. The γ densities are calculated for a grid of points using a numerical third-order differentiation of the electron densities calculated by GAUSSIAN 98. The origin is chosen to be the molecular centre of mass, XY defines the molecular plane, and the longitudinal axis of the molecule is along the X -axis. The box dimensions ($-12 \leq x \leq 12$ Å, $-7 \leq y \leq 7$ Å and $-5 \leq z \leq 5$ Å) ensure that the γ values obtained by integration are within 1% of the FF results. The relationship between γ and $\rho^{(3)}(\mathbf{r})$ is explained by considering a simple example: a pair of localized γ densities with positive and negative values. The sign of the contribution to γ is positive when the direction from positive to negative γ density coincides with the positive direction of the coordinate system. The sign becomes negative in the opposite case. Moreover, the magnitude of the contribution associated with this pair of γ densities is proportional to the distance between them.

4. Results and discussion

The UBHandHLYP/6-31G* results show that the γ_{xxxx} (γ) values for PDPL and IDPL are 1255×10^3 and 2383×10^3 a.u., respectively. This enhancement of γ for IDPL as compared to that for PDPL is predicted to be caused by the extension of π -conjugation length and the increase in the diradical character ($\gamma = 0.5833$ for PDPL and $\gamma = 0.7461$ for IDPL). PY2, which is a closed-shell system, is found to give a much smaller γ value (194×10^3 a.u.) than those of PDPL and IDPL (the ratio of γ : PDPL/PY2 = 6.47 and IDPL/PY2 = 12.3). This feature reconfirms that singlet diradical molecules with intermediate and somewhat large diradical characters tend to give about one-order larger γ value than closed-shell systems with similar π -conjugation size.

Fig. 2 shows the spin density distributions for PDPL (a) and IDPL (b), in which positive and negative densities represent α and β spin densities concerning π -electrons, respectively. Due to applying the spin unrestricted method, we obtain a symmetry broken spatial distribution concerning α and β spin distributions. Although such distribution is not observed in real systems, this can be interpreted to approximately indicate the feature of spatial correlation between α and β spins. Primary spin distributions of α and β spin densities are separated into two phenalenyl regions, respectively. For PDPL, major α spin densities are distributed on the right-hand phenalenyl unit (sites 1, 5, 8, 11, 19 and 26 (see Fig. 1)), while major β spin densities are done on the left-hand side unit (sites 10, 18, 25, 12, 20 and 27) though spin polarizations are observed in both phenalenyl units. Similar features are observed for IDPL: primary α and β spin densities are distributed on the right- (sites 7, 15, 23, 9, 17 and 25) and left- (sites 8, 16, 24, 10, 18 and 26) hand side phenalenyl units, respectively. These features of spin density distributions and intermediate diradical characters ($\gamma = 0.5833$ for PDPL and $\gamma = 0.7461$ for IDPL) suggest that spin-polarized α and β π -electrons tend to provide a large field-induced fluctuation between both end phenalenyl units, leading to large (hyper)polarizabilities in the longitudinal direction.

The γ density distributions for these molecules are shown in Fig. 3. For all systems, main contributions are turned out to come from π -electrons, whose contributions have opposite sign to those of σ -electrons. For PDPL

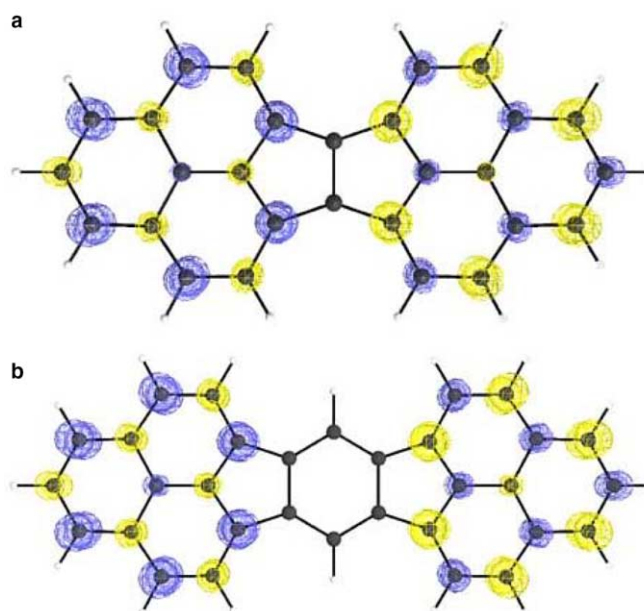


Fig. 2. Spin density distributions of open-shell singlet states of PDPL (a) and IDPL (b) evaluated at the level of UBHandHLYP/6-31G* treatment. The yellow and blue meshes represent α and β spin densities with iso-surface 0.01 a.u., respectively. These spin densities represent spatial spin correlations between α and β spin. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

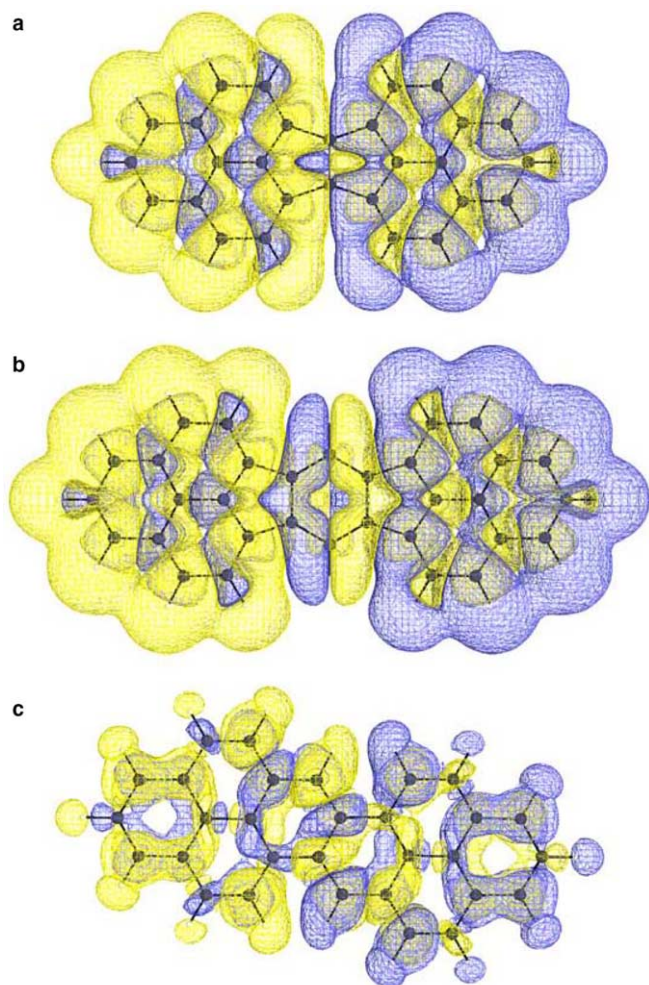


Fig. 3. γ density distributions for total electron contributions of the singlet states of PDPL (a), IDPL (b) and PY2 (c) determined at the BHandHLYP level. The yellow and blue meshes represent positive and negative γ densities with iso-surfaces with ± 100 a.u. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and IDPL, extended positive and negative γ densities are distributed on the left and right phenalenyl regions, respectively, which provide a dominant positive contribution to γ (see Section 3) though small opposite (negative) contributions appear in the central regions (sites 9 and 28 for PDPL and sites 1, 2, 3, 4, 5 and 6 for IDPL). It is found for PDPL and IDPL that the sites with dominant γ density distributions on phenalenyl units coincide with those with major spin densities. This supports our prediction that the spin polarized π -electrons concerning left- and right-hand phenalenyl units are the origin of the enhancement of γ values for these diradical molecules. The sign of γ densities on phenalenyl units is also found to change alternately in accordance with the variation of spin densities. In contrast to the dominant extended γ densities with positive contributions for PDPL and IDPL, the magnitudes of γ density distributions for PY2 are smaller and positive and negative γ densities appear alternately in the bond-length alternated

(Kekulé structured) region (18-14-8-6-1-2-5-7-12-17), the feature of which is also observed for closed-shell polyene chains, though both-end benzene ring regions provide positive contribution to γ . This alternate change of sign of γ densities in the longitudinal direction, which is not observed for PDPL and IDPL, is found to significantly reduce the positive contribution to γ for PY2. The large enhancement of magnitude of γ density and spatially well-separated positive and negative γ densities on both end phenalenyl regions for PDPL and IDPL turn out to be the origin of the significant enhancement of γ value for diradical molecules with intermediate diradical character as compared to closed-shell π -conjugated systems.

We here briefly explain the origin of the diradical character dependence of γ observed in the present and previous studies [2,5] based on the perturbation formula using the most simplified three-state model for a two-electron singlet diradical system. As is well known [11], a dominant contribution to γ for symmetric π -conjugated systems is in proportion to the product of transition moments $(\mu_{g,e1})^2 (\mu_{e1,e2})^2$, where g, e1 and e2 indicate the ground, the first-excited and the second-excited states, respectively. For singlet diradical systems, state g consists of a dominant contribution of diradical component and a slight contribution of zwitterionic component, state e2 consists of a dominant contribution of zwitterionic component and a slight contribution of diradical component, and state e1 is well described by a zwitterionic component [18]. This leads to the fact that the magnitude of transition moment between states e1 and e2, which is characterized by the products of spatial distributions of their large zwitterionic components, is much larger than that between states e1 and g, which is characterized by the products of spatial distributions of large and small zwitterionic components, respectively, in states e1 and g. Because the relative increase of diradical component in state g corresponds to the relative increase of the zwitterionic component of state e2, $|\mu_{e1,e2}|$ and $|\mu_{g,e1}|$ increases and decreases, respectively, with the increase of diradical character of state g. As a result, the quantity $(\mu_{g,e1})^2 (\mu_{e1,e2})^2$ i.e., γ value, attains a maximum in the intermediate and somewhat large diradical character regions.

5. Concluding remarks

We have shown that the π -conjugated polycyclic molecules involving phenalenyl units with intermediate and somewhat large diradical characters, such as PDPL and IDPL exhibit about one-order larger γ values than closed-shell systems with similar size of π -conjugation length. It has also been turned out from the γ density and spin density distributions that the primary spatial contribution to γ value for the diradical systems comes from the field-induced polarization of π electrons on the regions with large polarized spin densities between both end phenalenyl units. This indicates that the spin polarization of diradical systems with intermediate diradical character is closely related to the significant enhancement of γ for these systems. From the

present results, the γ values of such phenalenyl radical systems are expected to be controlled through adjusting the diradical character by relevant chemical modifications [19–21]. Although the present study only predicts the enhancement of static γ value of phenalenyl diradical systems with intermediate and somewhat large diradical characters, these systems also have a potential of enhancing and/or controlling dynamic γ values, whose imaginary parts are the origin of the two photon absorption properties, by the chemical modifications tuning the diradical characters. The study toward this direction will be in progress in our laboratory.

Acknowledgment

This work was supported by Grant-in-Aid for Scientific Research (No. 14340184) from Japan Society for the Promotion of Science (JSPS).

References

- [1] M. Nakano, T. Nitta, K. Yamaguchi, B. Champagne, E. Botek, *J. Phys. Chem. A* 108 (2004) 4105.
- [2] M. Nakano, R. Kishi, T. Nitta, T. Kubo, K. Nakasuji, K. Kamada, K. Ohta, B. Champagne, E. Botek, K. Yamaguchi, *J. Phys. Chem. A* 109 (2005) 885.
- [3] B. Champagne, E. Botek, M. Nakano, T. Nitta, K. Yamaguchi, *J. Chem. Phys.* 122 (2005) 114315.
- [4] B. Champagne, E. Botek, O. Quinet, M. Nakano, R. Kishi, T. Nitta, K. Yamaguchi, *Chem. Phys. Lett.* 407 (2005) 372.
- [5] M. Nakano, H. Nagao, K. Yamaguchi, *Phys. Rev. A* 55 (1997) 1503.
- [6] M. Nakano, S. Yamada, R. Kishi, M. Takahata, T. Nitta, K. Yamaguchi, *J. Nonlinear Opt. Phys. Mat.* 13 (2004) 411.
- [7] K. Yamaguchi, in: R. Carbo, M. Klobukowski (Eds.), *Self-Consistent Field Theory and Applications*, Elsevier, Amsterdam, 1990, p. 727.
- [8] S. Yamanaka, M. Okumura, M. Nakano, K. Yamaguchi, *J. Mol. Struct.* 310 (1994) 205.
- [9] M. Nakano, R. Kishi, N. Nakagawa, T. Nitta, T. Kubo, K. Nakasuji, K. Kamada, K. Ohta, B. Champagne, E. Botek, K. Yamaguchi, *J. Nonlinear Opt. Quantum Opt.*, in press.
- [10] K. Nakasuji, T. Kubo, *Bull. Chem. Soc. Jpn.* 77 (2004) 1791.
- [11] M. Nakano, I. Shigemoto, S. Yamada, K. Yamaguchi, *J. Chem. Phys.* 103 (1995) 4175.
- [12] D. Herebian, K.E. Wieghardt, F. Neese, *J. Am. Chem. Soc.* 125 (2003) 10997.
- [13] M.J. Frisch et al., *GAUSSIAN 98*, Revision A.11, Gaussian Inc., Pittsburgh, PA, 1998.
- [14] G. Maroulis, *J. Chem. Phys.* 111 (1999) 583.
- [15] G. Maroulis, D. Xenides, U. Hohm, A. Loose, *J. Chem. Phys.* 115 (2001) 7957.
- [16] H.D. Cohen, C.C.J. Roothaan, *J. Chem. Phys.* 43 (1965) S34.
- [17] A. Willetts, J.E. Rice, D.M. Burland, D.P. Shelton, *J. Chem. Phys.* 97 (1992) 7590.
- [18] L. Salem, C. Ronland, *Angew. Chem., Int. Ed.* 11 (1972) 92.
- [19] D. Scheschkewitz, H. Amii, H. Gomitzka, W.W. Schoeller, D. Bourissou, G. Bertrand, *Science* 195 (2002) 1880.
- [20] D.R. McMasters, J. Wirz, *J. Am. Chem. Soc.* 123 (2001) 238.
- [21] H. Sugiyama, S. Ito, M. Yoshifuji, *Angew. Chem., Int. Ed.* 42 (2003) 3802.