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Theoretical study on the diradical characters and third-order nonlinear optical properties of cyclic thiazyl diradical compounds

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ABSTRACT

Using the spin-unrestricted density functional theory method, the relationship between the diradical characters (γ) and the longitudinal second hyperpolarizabilities (γ) has been investigated for several cyclic thiazyl compounds (TZs) and polyacenes (PAs) involving up to six fused rings ($N = 6$). It turns out that γ strongly depends on the substitution position of the nitrogen and sulfur atoms in the five-membered rings of TZs and that its increase with N depends on the substitution positions. The γ values of TZs show an enhancement for intermediate γ values and are significantly larger than those of PAs of similar size.

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1. Introduction

The molecular design of highly active third-order nonlinear optical (NLO) materials has been an attractive topic in materials science because of their innovative future applications in photonics and optoelectronics including ultra-capacity optical memory [1,2], ultrafast optical switching [3], fabrication of hyperfine structures [4] and so on. To enhance and/or control the second hyperpolarizability γ , which is the third-order NLO property at the molecular scale, several molecular design principles have been proposed based on experimental and theoretical investigations [5–8]. As a novel design principle for further enhancing γ , we have theoretically demonstrated that open-shell singlet systems with intermediate diradical characters [9–13] exhibit larger γ values than closed-shell and pure diradical systems of similar size. These theoretical predictions have been substantiated for various polycyclic aromatic hydrocarbons [14–20] and transition metal containing systems [21,22] by *ab initio* molecular orbital (MO) and density functional theory (DFT) calculations, as well as by experimental measurements of two-photon absorption [23,24] and third-harmonic generation [25]. These results have stimulated other experimental and theoretical investigations on the linear and nonlinear optical properties of singlet diradical compounds [26–30].

In this study, we examine cyclic thiazyl compounds, a type of condensed-ring diradicaloids involving heteroatoms, some of which have been synthesized and reported as stable radicals [31–37]. Although these thiazyl compounds have been investigated as potential constituents of molecular conductors and

molecular magnetic materials [34–37], there have been few studies on their NLO properties. In this Letter, using the spin-unrestricted DFT method, we therefore investigate 1°) the correlation between the diradical characters and the γ for several thiazyl compounds composed of five and six membered rings with different positions of sulfur (S) and nitrogen (N) atoms as well as 2°) the structure–diradical character relationships. These results contribute to clarifying the performance of thiazyl compounds as potential constituents of highly efficient open-shell third-order NLO materials.

2. Model systems and calculation methods

Figure 1 shows the structures of three families of cyclic thiazyl diradical (TZs) compounds (**a**(N)–**c**(N)), which involve nitrogen (N) and sulfur (S) atoms at different positions in the five-membered rings, as well as of polyacenes (PA(N s)), where N denotes the number of fused rings including the terminal five- or six-membered rings. The results of PAs were obtained from our previous paper [20]. The geometries of all systems in their singlet states were optimized by the spin-unrestricted (U) B3LYP/6–311G* method. The C_{2h} , C_{2v} and D_{2h} symmetries were adopted for compounds **a**(N), **b**(N) and **c**(N), respectively. From the vibrational analysis, each structure was confirmed to be a minimum on the potential energy surface whereas relaxing the symmetry constraint did not lead to a more stable structure. Although the present method predicts that the ground states of these compounds with $N = 3$ are singlets when using the singlet optimized structures, the triplet states of **b**(3) and **c**(3) are found to be close to their singlet states (vertical singlet–triplet gaps attain 0.025 and 0.080 eV, respectively) (see [Supplementary data](#) for other systems and for different N values).

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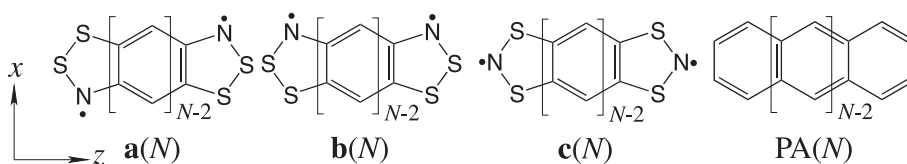


Figure 1. Molecular structures of the cyclic thiazyl diradical compounds [a(N), b(N), c(N)] as well as of the polyacenes [PA(N)], where N is the number of fused-rings. The coordinate axes are also shown.

In this study, since we focus on the relationship between the diradical character, the molecular size and structures and the γ values, we examine the singlet states.

The diradical characters y and the odd electron densities [38–40], which characterize the spatial distributions of unpaired electrons, were calculated using the LC-UBLYP/6–31G* method with a range separating parameter $\mu = 0.33$. The y values are defined by the occupation numbers (n_k) of the lowest unoccupied natural orbitals (LUNOs) [40]:

$$y = n_{\text{LUNO}} = 2 - n_{\text{HONO}}, \quad (1)$$

which takes a value between 0 (closed-shell) and 1 (pure diradical). The second equality, which represents the relation to the occupation number of the highest occupied natural orbital (HONO), is satisfied for single-determinant wavefunctions like those evaluated with the spin-unrestricted Hartree–Fock and density functional theory (DFT) methods. The diradical character y can be described by the spatial distribution of the odd electron densities $D_y^{\text{odd}}(\mathbf{r})$ obtained from [40]

$$D_y^{\text{odd}}(\mathbf{r}) = D_{\text{HONO}}^{\text{odd}}(\mathbf{r}) + D_{\text{LUNO}}^{\text{odd}}(\mathbf{r}), \quad (2)$$

where the odd electron density of the k th NO is defined by [39]

$$D_k^{\text{odd}}(\mathbf{r}) = \min(2 - n_k, n_k) \phi_k^*(\mathbf{r}) \phi_k(\mathbf{r}). \quad (3)$$

Here, $\min(2 - n_k, n_k)$ can be regarded as the probability for the electron of being unpaired in $\phi_k(\mathbf{r})$. In the present case, the diradical character y is expressed as [40]

$$y = \frac{1}{2} \text{Tr} [D_y^{\text{odd}}(\mathbf{r})]. \quad (4)$$

In order to calculate the longitudinal static γ (γ_{zzzz}), which is the dominant component of γ and is expected to be correlated to the diradical characters of TZs, we employed the finite-field (FF) method with the LC-UBLYP exchange–correlation functional, which was found to semi-quantitatively reproduce the γ values of open-shell singlet organic molecules at highly-correlated *ab initio* MO levels of approximation like the UCCSD(T) approximation [41]. As to the choice of basis set, although for small compounds, the use of extended basis sets including several sets of polarization and diffuse functions is required, even for obtaining qualitative γ values [42–44], the standard 6–31G* basis set was adopted since such basis set is expected to provide semiquantitative description of, at least, the longitudinal (dominant) γ component in extended π -conjugated systems [45,46]. Indeed, this choice is partly substantiated by previous results, showing that the 6–31G* basis set reproduces within 10% the γ value of s-indaceno[1,2,3-cd;5,6,7-c'd']diphenylene (IDPL), calculated using the 6–31G* + diffuse p ($\zeta = 0.0523$) basis set [14], which, in turn, is known to reproduce γ of large open-shell systems determined at highly correlated levels of approximation using more extended basis sets [43,46], though further confirmation of the validity of applying such basis sets to the evaluation of γ for π -conjugated systems involving heavier main group elements is needed. In this Letter, γ is calculated by

the fourth-order numerical differentiation of the energy with respect to external static electric field. All calculations were performed using the GAUSSIAN 09 package [47].

3. Results and discussion

3.1. Structures and diradical characters

Figure 2 shows the resonance structures (a) of three types of TZs, a(N)–c(N), and of PA(6) as well as several bond lengths of a(3)–c(3) (b). As seen from Figure 2a and b, the red bold C–C bonds (referred to as R) in the central 6-membered rings are formally represented as pure single bonds in the closed-shell forms, while they are predicted to take intermediate character between the single and double bonds in the open-shell forms. Thus, the compounds with a shorter R tend to have larger y since a benzenoid structure appears in the central 6-membered ring of the diradical form, while a quinoid or charge separated structure in the closed-shell form. As seen from Table 1, R decreases in the order: a(3) > b(3) > c(3), which indicates that the contribution of the closed-shell forms decreases in the same order. This is understood as follows. As shown in Figure 2, the closed-shell form of b(N) exhibits a charge separation between upper and lower zigzag edges, and that of c(N) presents hypervalent bonds between S, N and C atoms, both features of which tend to destabilize the closed-shell as compared to the open-shell forms. This suggests that compounds b(N) and c(N) favor more the open-shell forms over the closed-shell forms than a(N).

Figure 3 shows the distribution of odd electron densities $D_y^{\text{odd}}(\mathbf{r})$ of a(6)–c(6) and PA(6). The largest $D_y^{\text{odd}}(\mathbf{r})$ densities of a(6) are distributed on the N atoms of the terminal rings as well as on the attached zigzag edges with decreasing amplitudes as going from the N atoms to the central region. For b(6) and c(6), the largest $D_y^{\text{odd}}(\mathbf{r})$ intensities are also distributed on the N atoms as well as on the adjacent S atoms. Thus, the $D_y^{\text{odd}}(\mathbf{r})$ distributions of b(6) are located on the upper zigzag edge, while c(6) has negligible distributions on these edges. The odd electron density distributions reflect the primary spin polarization direction or effective covalent-like interaction, which is along the line joining the two radical sites in the major resonance structures, while their amplitudes determine the y values [a(6) ($y = 0.740$) < b(6) ($y = 0.959$) ~ c(6) ($y = 0.963$)]. In contrast, for PA(6), $D_y^{\text{odd}}(\mathbf{r})$ with much smaller amplitudes are distributed on both zigzag edges with the largest amplitudes in the central regions. This feature is understood by the open-shell resonance structure of PA(6), where the line joining the two radicals is along the x -axis as shown in Figure 2a.

Figure 4 shows the evolution of y as a function of N for TZs a(N)–c(N) and PA(N)s ($3 \leq N \leq 6$) (see also Table S1 in Supplementary data). For all systems, y increases with N . In a(N), y goes from 0.1 ($N = 3$) to ~0.7 ($N = 6$), while in b(N) and c(N), y is already large (>0.7) for the smallest compounds. Therefore, for $N = 4$ –6, a(N) belong to the intermediate y region, while b(N) and c(N) are nearly pure diradicals. These increases of y with N are governed by the distance between the terminal radical sites, which increases. On the other hand, small size PAs ($N < 5$) are closed-shell systems,

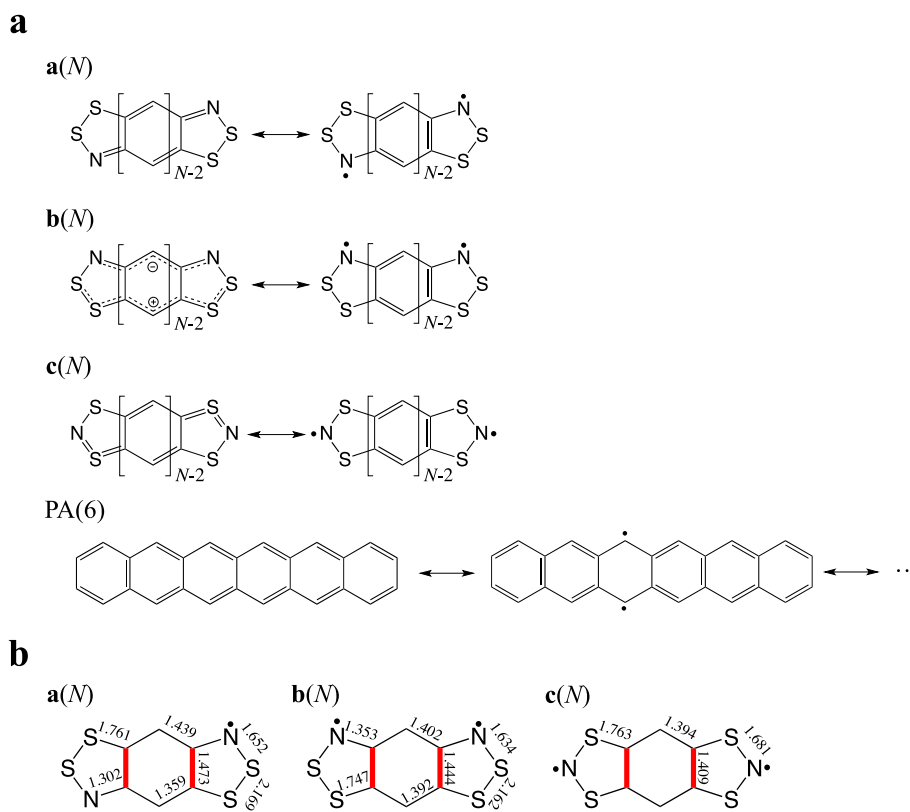


Figure 2. Resonance structures of **a(N)**, **b(N)** and **c(N)**, and of **PA(6)** (a) as well as representative optimized bond lengths (Å) (b).

Table 1

C–C bond lengths (*R*) marked by red bold bonds in Figure 2b and diradical characters *y* for TZs **a(3)**, **b(3)** and **c(3)**.

| | <i>R</i> (Å) | <i>y</i> (–) |
|-------------|--------------|--------------|
| a(3) | 1.473 | 0.081 |
| b(3) | 1.444 | 0.722 |
| c(3) | 1.409 | 0.863 |

while a finite diradical character appears from $N = 5$ and increases with N . This is ascribed to the longitudinal extension of π -conjugation on both zigzag edges, which causes the reduction of the energy gap between the highest molecular orbital (HOMO) (with bonding interaction between the mutually facing carbon (C) atoms) and the lowest unoccupied MO (LUMO).

3.2. Relationship between γ and γ

Figure 5 shows the size dependences of γ/N (longitudinal γ values per fused-ring) for TZs **a(N)**–**c(N)** and **PA(N)** where $3 \leq N \leq 6$ (see also Table S2 in Supplementary data). The γ/N values of **a(N)**–**c(N)** are larger than those of **PA(N)** at each N ($3 \leq N \leq 6$). Since for a given N , the π -conjugation lengths are similar for the TZs and PAs, these differences originate from the differences in the amplitudes and in the directions of the effective covalent-like interactions between odd electron densities contributing to the diradical characters. Namely, as predicted from the direction of the effective covalent-like interactions between the primary odd electron densities mentioned in Section 3.1, a diradical character based enhancement of γ are observed for **a(N)**, **b(N)**, and **c(N)**, while not for **PA(N)**s, which can be regarded as closed-shell

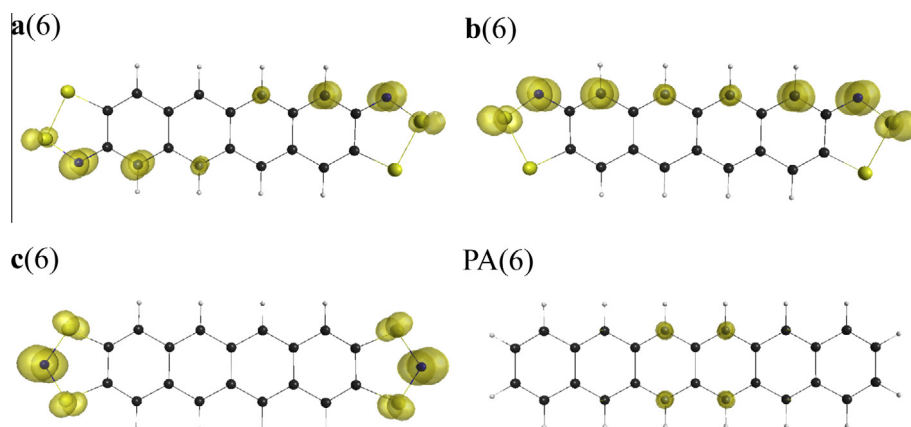


Figure 3. Odd electron density distributions (with isocontour of 0.003 a.u.) for γ of **a(6)**, **b(6)**, **c(6)**, and **PA(6)** calculated using the LC-UBLYP($\mu = 0.33$)/6–31G* method.

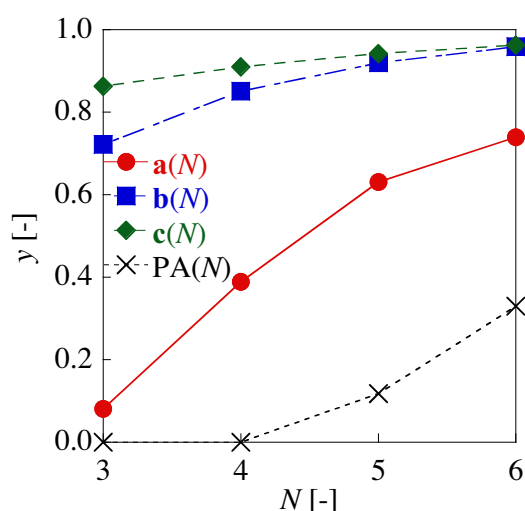


Figure 4. Evolution of the diradical character (y) as a function of N for $a(N)$, $b(N)$, $c(N)$, and $PA(N)$ ($3 \leq N \leq 6$).

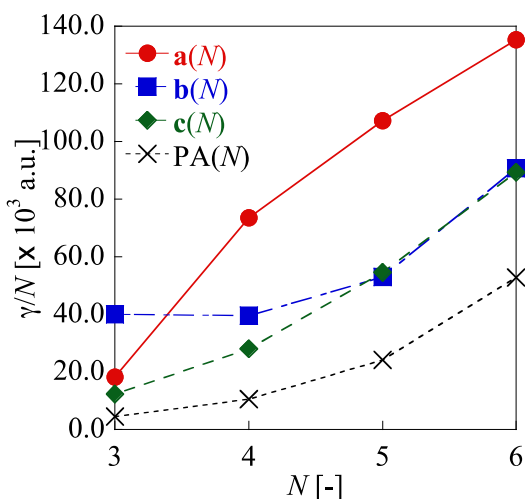


Figure 5. Size dependences of γ values per fused-ring unit (γ/N) for $a(6)$, $b(6)$, $c(6)$, and $PA(6)$ calculated using the LC-UBLYP($\mu = 0.33$)/6–31G* method.

systems along the z-axis direction. Thus, for TZs $a(N)$ – $c(N)$, the amplitude of γ/N and its evolution as a function of N are more sensitive than those for $PA(N)$ s.

For $N = 3$, the γ/N values of TZs are shown to increase in the order: $c(3)$ ($\gamma = 3.68 \times 10^4$ a.u.) < $a(3)$ ($\gamma = 5.47 \times 10^4$ a.u.) < $b(3)$ ($\gamma = 1.20 \times 10^5$ a.u.), which is consistent with the y – γ correlation, i.e., $y(a(3)) (=0.081) < y(b(3)) (=0.722) < y(c(3)) (=0.863)$. Similarly, for $4 \leq N \leq 6$, $a(N)$ exhibit the largest γ/N values among the present TZs. This is understood by the fact that for $4 \leq N \leq 6$, the $a(N)$ have intermediate y values ranging from ~ 0.4 to ~ 0.7 , while $b(N)$ and $c(N)$ have large y close to 1. For PAs, the increase of γ/N with N is only attributed to the extension of π -conjugation length since $PA(N)$ s are regarded as closed-shell systems along the z-axis direction. On the other hand, the size dependences of γ/N for TZs are caused by both the variation in diradical characters and the increase of the effective distance between the two radical centers [11]. Especially, we observe a large γ/N enhancement from $a(3)$ to $a(4)$. This is caused by the increase in the effective diradical distance but mostly by the increase of y from nearly closed-shell to intermediate diradical region [$a(3)$ ($y = 0.081$), $a(4)$ ($y = 0.389$)]. In contrast, the variation of γ/N from $b(3)$ to $b(4)$ is negligible. Indeed, although the increase in the effective diradical distance

would enhance γ/N if keeping the same y value, the increase of y from intermediate to nearly one [$b(3)$ ($y = 0.722$), $b(4)$ ($y = 0.851$)] damps γ/N so that it counteracts the other effect.

4. Concluding remarks

LC-UBLYP calculations have shown that the longitudinal γ of cyclic thiazyl compounds are larger than those of PAs owing to their intermediate y value. This behavior is associated with the odd electron densities that appear in the terminal five-membered rings, and is consistent with previous interpretations [20]. For all systems, γ increases as a function of the system size though the relative increase is different from each other. This is understood by the evolution of y and of the effective diradical distance as well as by the direction of the effective covalent-like interaction between the two radical sites.

We also found that the relative y values can be qualitatively estimated from the geometries in relation with the topology of the resonance structures. Indeed, these geometries account for $a(N)$ with a smaller y than $b(N)$ and $c(N)$ since the closed-shell forms in the resonance structures of $b(N)$ and $c(N)$, having charge separation between upper and lower zigzag edges and hypervalent bonds between S, N and C atoms, respectively, are detrimental to the stability of the systems. Therefore, y increases in the order: $a(3) < b(3) < c(3)$, consistently with the geometries.

These results demonstrate that the diradical character based design principle for enhancing/controlling γ in pure hydrocarbons can also be applied to cyclic thiazyl diradical compounds involving heteroatoms.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2013.08.087>.

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