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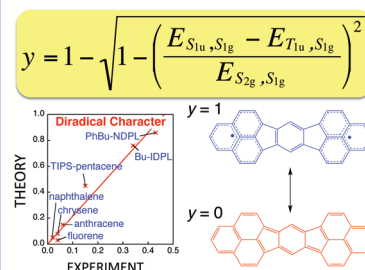
# Singlet Diradical Character from Experiment

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**ABSTRACT** Understanding the electronic structure of the singlet diradical state tackles the fundamentals of the chemical bond itself. The singlet diradical character is a key factor, which determines the chemical reactivity, the reaction products, as well as the chemical/physical (electronic, optical and magnetic) properties, although this quantity is defined in a purely theoretical manner. In this Letter, on the basis of the valence configuration interaction scheme, we present an explicit connection between the singlet diradical character and measured quantities obtained from one- and two-photon absorption spectra as well as from phosphorescence and electron spin resonance peaks. This enables us to estimate the singlet diradical character experimentally.

**SECTION** Molecular Structure, Quantum Chemistry, General Theory



Understanding the electronic structure of the singlet diradical state tackles the fundamentals of the chemical bond itself. While its simplest form refers to the variation of the covalent character in a stretched  $H_2$  molecule, singlet diradical states are also involved in organic chemical reactions, stereoselectivity and lifetime of short-lived intermediates,<sup>1–5</sup> inorganic four-membered heterocyclic compounds,<sup>6–8</sup> thermal sigmatropic migrations such as Cope rearrangement,<sup>9,10</sup> efficient singlet fission chromophores for dye-sensitized solar cells,<sup>11</sup> and so on. Optical transition from singlet diradical to zwitterionic state was also observed for the biphenanthrenylidene twisted olefin.<sup>12</sup> Moreover, various control schemes of spin multiplicity and open-shell character are experimentally obtained in diradicals and multiradicals, e.g., polynitrenes and nitreno-radicals,<sup>13</sup> spiro-fused oligo(triaryl-amine)s,<sup>14</sup> and diarylethene with nitronyl nitroxide radicals.<sup>15</sup> In the solid state, recent studies on thermodynamically stabilized singlet diradicals have demonstrated the coexistence of intra- and intermolecular covalent bonds originating from the open-shell character of the constituent molecules.<sup>16,17</sup> On the basis of such a fundamental understanding, our interests have broadened to functional properties originating from the singlet diradical electronic structure. Recently, we have theoretically assessed the third-order nonlinear optical (NLO) properties of singlet diradical molecules<sup>18–22</sup> and have found that their second hyperpolarizability  $\gamma$ —the molecular property at the origin of the third-order NLO responses—exhibits a bell-shape dependence as a function of the diradical character. This relationship has been explained by adopting a valence configuration interaction (VCI) method using a two-site system<sup>18</sup> and has been substantiated by ab initio molecular orbital and density functional theory calculations on several model and

real molecular systems, including the  $H_2$  dissociation<sup>18</sup> and  $p$ -quinodimethane<sup>18</sup> models, and a family of thermally stable diphenalenyl diradical systems.<sup>19</sup> These theoretical predictions have been confirmed by two-photon absorption (TPA) measurements 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).<sup>22</sup> In addition, it turns out that systems with intermediate diradical character exhibit remarkable spin state dependence of  $\gamma$ .<sup>20</sup>

As seen from these results, the diradical character is a key factor, which determines the chemical reactivity and physical properties (electronic, optical and magnetic), but so far, there have been no means of estimating this quantity experimentally. Namely, the diradical character is not an observable but can be theoretically defined as twice the weight of the double excitation configuration in the singlet ground state within the multiconfigurational self-consistent-field theory.<sup>23</sup> In this communication, we provide a connection between the diradical character and measured quantities, which opens a path to an experimental estimation of the singlet diradical character.

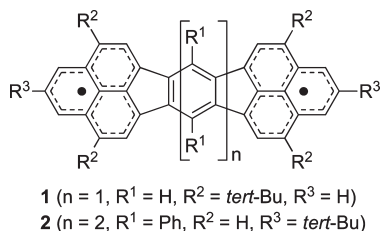
From our previous study based on the VCI scheme using a simple two-site system  $A^\bullet - B^\bullet$  with two electrons in two orbitals,<sup>21</sup> the analytical form of the diradical character  $y$  reads as  $y = 1 - 4|t|/(U^2 + 16t^2)^{1/2}$ , where  $U$  represents the difference between on-site and intersite Coulomb integrals, and  $t$  is a transfer integral using the localized natural orbital basis. This formula is alternatively expressed as (see the Supporting

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**Scheme 1.** Structures of Singlet Diradical Compounds



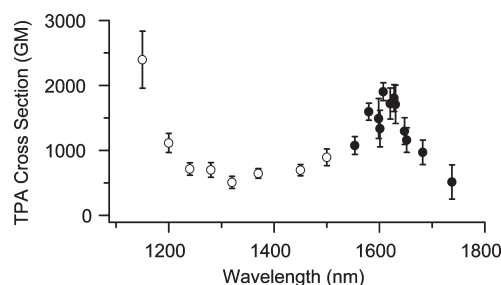
Information for the derivation)

$$y = 1 - \sqrt{1 - \left( \frac{{}^1E_{1u} - {}^3E_{1u}}{{}^1E_{2g} - {}^1E_{1g}} \right)^2}$$

$$= 1 - \sqrt{1 - \left( \frac{E_{S_{1u}, S_{1g}} - E_{T_{1u}, S_{1g}}}{E_{S_{2g}, S_{1g}}} \right)^2} \quad (1)$$

where the first right-hand side (rhs) involves the energies of the four electronic states: an essentially neutral lowest-energy singlet state of g symmetry  $|S_{1g}\rangle$  (of energy  ${}^1E_{1g}$ ), an ionic singlet state with u symmetry  $|S_{1u}\rangle$  (of energy  ${}^1E_{1u}$ ), another singlet state of g symmetry but essentially ionic  $|S_{2g}\rangle$  (of energy  ${}^1E_{2g}$ ), and a neutral triplet state  $|T_{1u}\rangle$  (of energy  ${}^3E_{1u}$ ).<sup>21,24</sup> In the second rhs,  $E_{S_{2g}, S_{1g}} (\equiv {}^1E_{2g} - {}^1E_{1g})$ ,  $E_{S_{1u}, S_{1g}} (\equiv {}^1E_{1u} - {}^1E_{1g})$  and  $E_{T_{1u}, S_{1g}} (\equiv {}^3E_{1u} - {}^1E_{1g})$  correspond to the excitation energies of the higher singlet state of g symmetry (two-photon allowed excited state), of the lower singlet state with u symmetry (one-photon allowed excited state), and of the triplet state with u symmetry, respectively. Following refs 21 and 24, when  $U$  is small,  ${}^1E_{1u}$  approaches  ${}^3E_{1u}$ , so that  $y$  tends to be 0 since  ${}^1E_{1u} - {}^3E_{1u} \approx 0$ . On the contrary, when  $U$  is large ( $U \gg |t|$ ),  ${}^1E_{2g}$  and  ${}^1E_{1u}$  tend to become degenerate, while  $E_{S_{1u}, S_{1g}} \gg E_{T_{1u}, S_{1g}}$ , leading to  $y = 1$  (see eq 1). Obviously, all parameters in the second rhs are experimentally accessible.  $E_{S_{1u}, S_{1g}}$  and  $E_{S_{2g}, S_{1g}}$  correspond to the lowest-energy peaks of the one- and two-photon absorption spectra, respectively, while  $E_{T_{1u}, S_{1g}}$  can be obtained from phosphorescence and electron spin resonance (ESR) measurement.

Thus, the experimental determination of these three excitation energies is essential for the calculation of  $y$  based on eq 1. However, two-photon transition energies of molecules having intermediate diradical character have not yet been reported, except in our previous study.<sup>22</sup> In that work, we reported the TPA spectrum of *tert*-butyl-substituted IDPL (**1**, Scheme 1) and NDPL (**2**) measured by the femtosecond open-aperture Z-scan method.<sup>22</sup> These compounds were found to have characteristically low transition energies: the TPA peak of **1** was located at 1425 nm. On the other hand, **2** exhibited an increase in a TPA cross section as the wavelength increased, but the peak was not reached even in the long-wavelength limit of the setup (1500 nm), suggesting that its transition energy is lower than in **1**. Therefore we improved our setup to extend the measurement wavelength range up to 1750 nm. Then, by using the same procedure,<sup>22</sup> the TPA peak was found to be located at 1610 nm (Figure 1, corresponding to the two-photon excitation energy of 1.54 eV) for a solution



**Figure 1.** TPA spectrum of **2** in chloroform measured by the open-aperture Z-scan (●) together with previously reported data points (O, from ref 22).

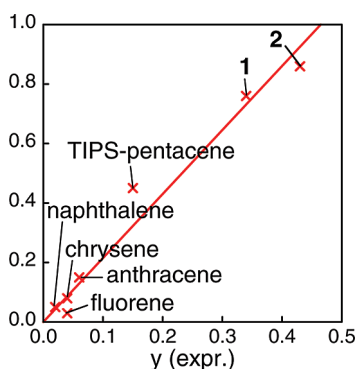
**Table 1.** Excitation Energies and the Diradical Character ( $y$ ) of the Compounds

compounds	$E_{S_{1u}, S_{1g}}/\text{eV}$	$E_{S_{2g}, S_{1g}}/\text{eV}$	$E_{T_{1u}, S_{1g}}/\text{eV}$	$y$	
				expr.	theor. <sup>a</sup>
<b>1</b>	1.62 <sup>b</sup>	1.87 <sup>b</sup>	0.21 <sup>c</sup>	0.34	0.76 <sup>d</sup>
<b>2</b>	1.42 <sup>b</sup>	1.54 <sup>e</sup>	0.16 <sup>f</sup>	0.43	0.86 <sup>d</sup>
TIPS-pentacene	1.94 <sup>g</sup>	2.07 <sup>h</sup>	0.86 <sup>i</sup>	0.15	0.45 <sup>j</sup>
anthracene	3.42 <sup>k</sup>	4.44 <sup>k</sup>	1.87 <sup>k</sup>	0.06	0.15 <sup>d</sup>
naphthalene	3.97 <sup>k</sup>	5.22 <sup>k</sup>	3.00 <sup>k</sup>	0.02	0.05 <sup>d</sup>
chrysene	3.43 <sup>l</sup>	3.58 <sup>m</sup>	2.46 <sup>l</sup>	0.04	0.08 <sup>d</sup>
fluorene	4.12 <sup>l</sup>	4.22 <sup>n</sup>	2.93 <sup>l</sup>	0.04	0.03 <sup>d</sup>

<sup>a</sup>The method for calculating  $y$  from the UNOs is described in the Supporting Information. <sup>b</sup>In chloroform, ref 22. <sup>c</sup>From solid-state ESR data, ref 25. <sup>d</sup>Calculated from the occupation numbers of UNO/6-31G\*\* using the geometries optimized by the UB3LYP/6-31G\*\* method (see Figures 2S–7S in the Supporting Information). <sup>e</sup>In chloroform, this work. <sup>f</sup>From magnetic measurement data, ref 26. <sup>g</sup>In THF, this work. <sup>h</sup>In THF, Supporting Information of ref 22. <sup>i</sup>From measurement data on pentacene in tetracene crystal, ref 31. <sup>j</sup>Calculated from the UNO/6-31G\*\* occupation numbers using the geometry derived from the crystal structure where the isopropyl groups are replaced by H atoms (see Figure 8S in the Supporting Information), ref 32. <sup>k</sup>Reference 27 and the references herein. <sup>l</sup>Reference 28. <sup>m</sup>In crystal phase, ref 30. <sup>n</sup>In crystal phase, ref 29.

of **2** in chloroform (0.40 mM). Including this value, the experimentally obtained one- and two-photon excitation energies of **2** as well as **1** are listed in Table 1. The diradical characters  $y$  of these molecules were then calculated from eq 1 with combining these data with the  $E_{T_{1u}, S_{1g}}$  values determined from ESR and magnetic measurements.<sup>25,26</sup> The obtained  $y$  values are 0.34 (for **1**) and 0.42 (for **2**), corresponding to an intermediate diradical character as expected by the theoretical calculation; however, these values are nearly the half of the corresponding theoretically calculated ones (also in Table 1) from the occupation numbers of the spin-unrestricted Hartree–Fock natural orbitals (UNOs). This result on **1** and **2** suggests some scaling between the experimentally deduced and theoretically calculated  $y$  values.

Therefore, we also determined  $y$  for some closed-shell aromatic hydrocarbons (also in Table 1) in order to test further the range of validity of eq 1. The experimental  $E_{S_{1u}, S_{1g}}$ ,  $E_{S_{2g}, S_{1g}}$  and  $E_{T_{1u}, S_{1g}}$  values were taken from the literature.<sup>27–31</sup> All closed-shell species exhibit  $y$  values smaller than 0.2, suggesting good applicability of eq 1. Clearly, the difference in  $y$



**Figure 2.** Experimentally deduced diradical characters  $y(\text{expr.})$  versus theoretically calculated  $y(\text{theor.})$  for several compounds (listed in Table 1) calculated from the occupation numbers of UNO/6-31G\*\*.

magnitude between the open- and closed-shell compounds of Table 1 originates from the energy separation between the first excited singlet and triplet states,  $E_{S_{1u},S_{1g}} - E_{T_{1u},S_{1g}}$ , and that between the second excited singlet and the ground singlet states,  $E_{S_{2g},S_{1g}}$ , as expected. The small but non-negligible  $y(\text{expr.})$  value of 6,13-bis(triisopropylsilyl)ethynyl-pentacene (TIPS-pentacene) suggests the weak open-shell nature of this compound.

Figure 2 illustrates the comparison of the experimentally deduced  $y$  values to the theoretically calculated ones. We can observe a significant correlation between the experimental and theoretical results for all compounds treated here in spite of the difference in the scales, which can originate from several factors, including the effects of the environment (solvation or crystal packing), inconsistencies among the different experimental methods, and the approximate nature of the VCI model. Nevertheless, such qualitative agreement between the experimentally deduced and theoretically calculated  $y$  values supports the validity of eq 1. Further testing of eq 1 for its comprehensive applicability with many data points is now in progress.

In summary, the theoretical relationship between the diradical character and measurable quantities (eq 1) turns out to provide qualitative (and, after scaling, semiquantitative) estimates for the diradical characters, which are theoretically calculated from the UNOs occupation numbers.

**SUPPORTING INFORMATION AVAILABLE** Derivation of eq 1 as well as its illustration in the case of a two-site model like the stretched  $H_2$  molecule, description of the method for calculating the diradical character, and geometries of the compounds listed in Table 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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