# Are Fully Conjugated Expanded Indenofluorenes Analogues and Diindeno[n]thiophene Derivatives Diradicals? A Simplified (Spin-Flip) Time-Dependent Density Functional Theory [(SF-)sTD-DFT] Study

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**ABSTRACT:** Polycyclic hydrocarbons are often used to understand the electronic structure of nanographene systems. Among them, indeno [1,2b] fluorene and indeno[1,2c] fluorene isomers present a central p-quinodimethane unit leading to unique optical properties. In this work, we characterized the absorption spectra of indeno[1,2b] fluorene and [2,1-c] diindeno[n] thiophene derivatives with (spin-flip) simplified time-dependent density functional theory [(SF-)sTD-DFT] methods. Note that the SF-sTD-DFT level of theory allows a computationally efficient treatment for large diradicals. To interpret spectra, we implemented natural transition orbitals (NTOs) at both SF-sTD-DFT and sTD-DFT levels. This compact and method-independent representation of the



electronic excitation provides a simple interpretation for the low-lying excited states of this set of molecules in terms of three different types of NTOs: "quinoid", "aromatic", and " $\pi$ -bonded". When comparing with experiment, we found that only one molecule of this set is actually a high-spin triplet diradical. Others are almost closed-shell molecules with a very small contribution from a doubly excited configuration that only the spin-flip method could capture. The small amount of static correlation recovered by the spin-flip active space provides a linear relation between the first visible theoretical and experimental excitation energies among this set.

# I. INTRODUCTION

A diradical is a molecule that contains two nearly degenerate singly occupied molecular orbitals (SOMOs).<sup>1</sup> To create a diradical from a benzene molecule that has a degenerate  $\pi$ -conjugated orbital, one just needs to lift the degeneracy, replacing two hydrogens by, e.g., two CH<sub>2</sub> groups. Figure 1



Figure 1. Two frontier molecular orbitals of *p*-quinodimethane.

presents the resulting two nearly degenerate frontier molecular orbitals (MOs) of *p*-quinodimethane (PQM). Because of their shapes, the first MO could be called the "quinoid" MO and the second the "aromatic" MO. Their energy separation is obviously geometry-dependent. Increasing the length of the two exocyclic carbon–carbon bonds will favor a diradical ground state, while the reverse will favor the quinoidal form. From linear combinations of configurations obtained by distributing two electrons in two nearly degenerate molecular orbitals (Figure 2), six wave functions that are eigenfunctions of the  $\hat{S}^2$  operator are possible:

| $\phi_2 + \phi_1 + \phi_1 + \phi_1 + \phi_1 + \phi_2 + \phi_1 $ | $\rightarrow$   | $\stackrel{\longrightarrow}{\uparrow}$  | $\stackrel{\uparrow}{\longrightarrow}$   | ${\uparrow \downarrow}$   | $\stackrel{\uparrow\downarrow}{=}$   |
|---|---|---|--|---|--|
| $\begin{cases} \phi_1 \phi_2 \alpha \alpha \\ \phi_2 \phi_1 \alpha \alpha \end{cases}$  | $egin{cases} \phi_1\phi_2etaeta\ \phi_2\phi_1etaeta$ $\phi_2\phi_1etaeta$ | $\begin{cases} \phi_1 \phi_2 \alpha \beta \\ \phi_2 \phi_1 \beta \alpha \end{cases}$  | $\begin{cases} \phi_1 \phi_2 \beta \alpha \\ \phi_2 \phi_1 \alpha \beta \end{cases}$ | $\left\{egin{array}{l} \phi_1\phi_1lphaeta\ \phi_1\phi_1etalpha$  | $\begin{cases} \phi_2 \phi_2 \alpha \beta \\ \phi_2 \phi_2 \beta \alpha \end{cases}$ |
| $\Downarrow$  | $\Downarrow$  | $\qquad \qquad $ |  | $\qquad \qquad $ |  |
| ${}^{3}\Psi_{A}$  | ${}^{3}\Psi_{B}$  | ${}^{3}\Psi_{C}, {}^{1}\Psi_{D}$  |  | ${}^{1}\Psi_{E}, {}^{1}\Psi_{F}$  |  |

**Figure 2.** Six configurations obtained by distributing two electrons in two nearly degenerate molecular orbitals. Their linear combinations lead to six spin-pure diradical wave functions.

$${}^{3}\Psi_{A} = \frac{1}{\sqrt{2}} (\phi_{1}\phi_{2} - \phi_{2}\phi_{1})(\alpha\alpha)$$
(1)

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$${}^{3}\Psi_{B} = \frac{1}{\sqrt{2}} (\phi_{1}\phi_{2} - \phi_{2}\phi_{1})(\beta\beta)$$
(2)

$${}^{3}\Psi_{C} = \frac{1}{2}(\phi_{1}\phi_{2} - \phi_{2}\phi_{1})(\alpha\beta + \beta\alpha)$$
(3)

$${}^{1}\Psi_{D} = \frac{1}{2}(\phi_{1}\phi_{2} + \phi_{2}\phi_{1})(\alpha\beta - \beta\alpha)$$

$$(4)$$

$${}^{1}\Psi_{E} = \frac{1}{2\sqrt{1+\eta^{2}}} [(\phi_{1})^{2} - \eta(\phi_{2})^{2}](\alpha\beta - \beta\alpha)$$
(5)

$${}^{1}\Psi_{F} = \frac{1}{2\sqrt{1+\eta^{2}}} [\eta(\phi_{1})^{2} + (\phi_{2})^{2}](\alpha\beta - \beta\alpha)$$
(6)

While  ${}^{3}\Psi_{A}$  and  ${}^{3}\Psi_{B}$  are two high-spin triplet wave functions,  ${}^{3}\Psi_{C}$  is the low-spin triplet and  ${}^{1}\Psi_{D}$  the open-shell singlet wave function.  ${}^{1}\Psi_{E}$  and  ${}^{1}\Psi_{F}$  are diradical singlet wave functions, where  $\eta$  is a variational parameter related to their diradical character. Among diradical character definitions<sup>2-6</sup> based on the density matrix, Head-Gordon's diradical index<sup>4</sup> uses the spin-averaged occupation numbers  $\overline{n}_{i}$  of the natural orbitals and is defined as

$$n_{\rm u,nl} = \sum_{i} \overline{n}_{i}^{2} (2 - \overline{n}_{i})^{2}$$

$$\tag{7}$$

where *i* is the occupied natural orbital index, u stands for unpaired electrons, and nl stands for the nonlinear formulation of the diradical character by Head-Gordon. It represents the number of effectively unpaired electrons. Nanda and Krylov<sup>7</sup> provided a simple relation between  $n_{u,nl}$ and  $\eta$  for a two electrons in two molecular orbitals system:

$$n_{\rm u,nl} = \frac{32\eta^4}{(1+\eta^2)^4} \tag{8}$$

While exact for a two-electron system, this relation could approximate the diradical character for spin-flip states dominated by two leading closed-shell configurations when considering that the variational parameter  $\eta$  is the ratio

between weights of both configurations  $\left(\eta = \frac{|X_{\phi_1 \to \phi_2}|}{|X_{\phi_2 \to \phi_1}|}\right)$ .

Since they were isolated for the first time in 2004,<sup>8</sup> nanographene systems have become a sizable field of investigation. To characterize their electronic structure, model molecules like polycyclic hydrocarbons (PAHs) are often used.9 They are also promising candidates for applications in electronics, spintronics, and nonlinear optics.9-11 Among PAHs, four types of compounds could have a diradical ground state: (i) acenes, (ii) periacenes and anthenes, (iii) zethrenes, and (iv) extended PQM derivatives.  $^{12-19}$  In this contribution, we are interested in the last class of compounds in which PQM units are introduced into aromatic or antiaromatic systems to design possibly new highly conjugated hydrocarbon diradicals.<sup>12–19</sup> In this class, indenofluorenes<sup>15,17–19</sup> are 6-5-6-5-6 fully conjugated carbon rings in which five structural isomers are possible. Among them, only the indeno[1,2-b] fluorene and indeno[2,1-c]fluorene isomers have a central PQM unit (Figure 3). The presence of five-membered rings implies a reduction of symmetry with respect to six-membered ring analogues. This may lead to some unique optical properties. With their 20  $\pi$ electrons, indenofluorenes are antiaromatic according to





**Figure 3.** Quinoidal and possible diradical structures of the fully conjugated indeno[1,2-b]fluorene skeleton and its [2,1-c]diindeno-[1]thiophene analogue.

Hückel's rule. Resonance structures of the fully conjugated indeno[1,2-b] fluorene skeleton (Figure 3) show the possible existence of a diradical. Haley and co-workers<sup>18</sup> explored the chemical space of indeno [1,2-b] fluorene and quinoidal analogues by functional group substitutions and skeleton modifications/extensions. In particular, they produced dinaphthoindacene and diphenanthroindacene derivatives, kinetically stabilized by bulky mesityl (MES) groups.<sup>20</sup> They also substituted the PQM unit in the indeno[2,1-c] fluorene with a 2,5-dimethylidenethiophene (DMT) one (Figure 3), forming three [2,1-c] diindeno [n] thiophene derivatives with n= 1-3 thiophene units and containing two triisopropylsilyl (TIPS) groups.<sup>18,21</sup> Figure 4 presents the structures of the eight compounds studied in this article and taken from ref 18. Note that the identification number of each compound is the same as in the original publication.<sup>18</sup> The first set of compounds includes 11i, an indeno[1,2-b]fluorene, 20a, **21a**, and **22a**, three isomers of [1,2-b] dinaphthoindacene, and 23a, a diphenanthroindacene molecule, all substituted by two MES groups. The second set includes 27-29 that are three [2,1-c] diindeno [n] thiophene derivatives containing two TIPS groups. Indenofluorene derivatives are highly colored molecules; e.g., the 11i solution is orange and that of 27 dark green. Note that 27 and 29 belong to the  $C_{2\nu}$  point group and 28 belongs to the  $C_{2h}$  point group. While the  $\pi$ -conjugated pathway of the quinoidal core is enlarged, low-energy states are red-shifted with respect to 11i ones.<sup>18</sup> For the first set of compounds, Haley and co-workers<sup>18</sup> showed that the maximum wavelength of the lowest-energy absorption is progressively shifted to lower energies: from 11i (515 nm) to 21a (543 nm) to 20a (549 nm) to 22a (578 nm) to 23a (622 nm). The same effect is also observed within the second set (27-29). They also proposed that the alternation between axo- and centrosymmetry in the second set could be seen in the staggering of absorption edges. According to their calculations, when a symmetry inversion is present, the S<sub>0</sub> to S<sub>1</sub> transition is forbidden, while this is not the case when there is no inversion center.

The big question when dealing with PAHs is the identification of the open-shell nature of the compound. This usually requires extra experiments like electron spin resonance (ESR) or superconducting quantum interference device (SQUID) measurements in conjunction with quantum chemical calculations.<sup>19</sup> Inadequately, very often unrestricted mean-field electronic structure methods are used, resulting in

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Figure 4. Fully conjugated expanded indeno [1,2-b] fluorene analogues and [2,1-c] diindeno [n] thiophene (n = 1-3) derivative structures.

spin-contaminated solutions. Because of the near degeneracy of the SOMOs, the system should be described by a multiconfigurational wave function with strong contributions from (restricted) doubly excited determinants to describe  $\eta$ -dependent singlet diradical wave functions (see eqs 7 and 8 for a model with two electrons and two orbitals). Krylov<sup>22–25</sup> proposed to treat such systems with the efficient spin-flip (SF) method. It starts with a well-behaved high-spin ( $\alpha\alpha$ ) triplet state. Then, the target open-shell state is obtained by spin-flipping excitations. The resulting states are spin-pure for  ${}^{3}\Psi_{\rm C} - {}^{1}\Psi_{\rm F}$  kinds of wave functions. The SF-TD-DFT (time-dependent density functional theory) method describes excitation energies<sup>26–33</sup> with an accuracy similar to what is usually achieved by highly correlated methods.

Recently, we proposed a spin-flip version<sup>34</sup> of the simplified time-dependent density functional theory (sTD-DFT) method proposed by Grimme and co-workers<sup>35–37</sup> to treat large diradicals up to several thousand of atoms when considering its extended tight-binding (xTB) flavor. The key of this approach is to approximate the time-dependent part of the treatment by short-range damped Coulomb interactions of transition density monopoles to evaluate two-electron integrals. We used a benchmark set of nine diradicals to assess the performance of the SF-sTD-DFT method. This set included anthenes, zethrenes, and extended PQM derivatives.

Using the B5050LYP exchange correlation functional, we obtained a maximum averaged deviation of only 0.076 eV with respect to the unapproximated SF-TD-DFT level of theory. The computational effort was drastically reduced. We concluded that this method is well suited for the treatment of diradicals and reproduces their absorption spectra considering low-lying excited states with a small amount of spin contamination while higher excited states suffer from the inherent truncation of the singly excited space.

In this article, we use SF-sTD-DFT and sTD-DFT methods to compute absorption spectra for two sets of molecules selected from the work of Haley and co-workers.<sup>18</sup> It was recently shown that natural orbitals are rather useful for understanding the diradical character.<sup>38,39</sup> We introduce the (SF-)sTD-DFT implementation of natural transition orbitals<sup>40–45</sup> (NTOs) as an interpretation tool. NTOs provide a compact and method-independent representation of the electronic excitation. Its theoretical background is described in section II. NTOs are used in the framework of SF-TD-DFT and implemented to characterize state-to-state TD-DFT transitions. While computational details are provided in section III, section IV presents the results, and conclusions are given in section V.

# **II. THEORY**

In the following, p-s indices refer to general molecular orbitals, i-l to occupied molecular orbitals, and a-d to unoccupied molecular orbitals. To analyze excited state characters, a cumbersome and method-dependent approach is to resort to leading configurations and molecular orbitals. The analysis of the one-particle transition density matrix (1-TDM) provides a more rigorous way to approach this problem.<sup>40–45</sup> The 1-TDM between states *n* and *m* is defined as

$$\gamma_{pq}^{mn} = \sum_{\sigma} \langle m | p_{\sigma}^{\dagger} q_{\sigma} | n \rangle \tag{9}$$

where  $p_{\sigma}^{\dagger}$  and  $q_{\sigma}$  are the creation and annihilation operators corresponding to spin-orbitals  $\phi_{p\sigma}$  and  $\phi_{q\sigma}$  respectively. The 1-TDM contains all information to compute the one-electron transition moment between two states:

$$\mu_{mn} = \langle m | \mu | n \rangle = Tr[\gamma^{mn} \mu] \tag{10}$$

where  $\mu$  is the dipole moment matrix. In the density-based linear response TD-DFT formalism,<sup>46-52</sup> the 1-TDM between ground state 0 and an excited state *m* is defined as

$$\gamma_{ia}^{m0} = \left( X_{i_a a_a}^{m0} + Y_{i_a a_a}^{m0} \right) + \left( X_{i_\beta a_\beta}^{m0} + Y_{i_\beta a_\beta}^{m0} \right)$$
(11)

where  $X_{i_{\sigma}a_{\sigma}}^{m0}$  and  $Y_{i_{\sigma}a_{\sigma}}^{m0}$  are the excitation and deexcitation matrices, respectively. A compact representation of the electronic excitation can be obtained using singular-value decomposition (SVD) of both spin blocks of the 1-TDM:

$$\gamma^{m0} = \mathbf{U}_{\alpha} \boldsymbol{\Lambda}_{\alpha}^{m0} \mathbf{V}_{\alpha}^{T} + \mathbf{U}_{\beta} \boldsymbol{\Lambda}_{\beta}^{m0} \mathbf{V}_{\beta}^{T}$$
(12)

where U and V are unitary matrices and  $\Lambda$  is a diagonal matrix:

$$\Lambda_{\sigma}^{m0} = \operatorname{diag}(\sqrt{\lambda_{1}^{\sigma}}, \sqrt{\lambda_{2}^{\sigma}}, ...)$$
(13)

The advantage of this procedure is that only a few  $\lambda_i$  weighting coefficients are significant, leading to a compact representation of the excitation. For each  $\lambda_i$ , a pair of hole and electron NTOs is defined as

$$\begin{cases} \psi_{i_{\sigma}}^{\text{hole}}(r) = \sum_{j_{\sigma}} \mathbf{U}_{j_{\sigma}i_{\sigma}} \phi_{j_{\sigma}}(r) \\ \psi_{i_{\sigma}}^{\text{electr.}}(r) = \sum_{a_{\sigma}} \mathbf{V}_{a_{\sigma}i_{\sigma}} \phi_{a_{\alpha}}(r) \end{cases}$$
(14)

The participation ratio provides the number of significant NTOs:

$$PR_{NTO} = \frac{\left[\sum_{i} \left(\lambda_{i}^{\alpha} + \lambda_{i}^{\beta}\right)\right]^{2}}{\sum_{i} \left[\left(\lambda_{i}^{\alpha}\right)^{2} + \left(\lambda_{i}^{\beta}\right)^{2}\right]}$$
(15)

One can also describe the electron transition by an exciton quasi-particle defined on the basis of NTOs:

$$\chi(\vec{r}_h, \vec{r}_e) = \sum_{i\sigma} \sqrt{\lambda_i^{\sigma}} \psi_{i_{\sigma}}^{\text{hole}}(\vec{r}_h) \psi_{i_{\sigma}}^{\text{electr.}}(\vec{r}_e)$$
(16)

We recently showed that state-to-state transition dipole moments are easily derived from the double residue of the sTD-DFT quadratic response function:<sup>53,54</sup>

$$\langle m | \mu_{\xi} - \langle 0 | \mu_{\xi} | 0 \rangle | n \rangle$$

$$= \frac{1}{2} \sum_{\sigma} \left[ \sum_{\substack{a_{\sigma} i_{\sigma} j_{\sigma}}} (X_{i_{\sigma} a_{\sigma}}^{n0} \mu_{i_{\sigma} j_{\sigma}, \xi} X_{j_{\sigma} a_{\sigma}}^{m0} + Y_{i_{\sigma} a_{\sigma}}^{m0} \mu_{i_{\sigma} j_{\sigma}, \xi} Y_{j_{\sigma} a_{\sigma}}^{n0}) - \sum_{a_{\sigma} b_{\sigma} i_{\sigma}} (X_{i_{\sigma} a_{\sigma}}^{n0} \mu_{a_{\sigma} b_{\sigma}, \xi} X_{i_{\sigma} b_{\sigma}}^{m0} + Y_{i_{\sigma} a_{\sigma}}^{m0} \mu_{a_{\sigma} b_{\sigma}, \xi} Y_{i_{\sigma} b_{\sigma}}^{n0}) \right]$$

$$(17)$$

Note that this expression corresponds to the unrelaxed TD-DFT case. As previously shown by Furche,<sup>48</sup> the state-to-state TD-DFT 1-TDM is composed of the occupied–occupied (occ.) and unoccupied–unoccupied (unocc.) blocks:

$$\boldsymbol{\gamma}^{mn} = \begin{pmatrix} \boldsymbol{\gamma}_{\text{occ.}}^{mn} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{\gamma}_{\text{unocc.}}^{mn} \end{pmatrix}$$
(18)

where

$$\begin{aligned}
\varphi_{j_{j},\text{occ.}}^{mn} &= \sum_{a_{\alpha}} \left( X_{i_{\alpha}a_{\alpha}}^{m0} X_{j_{\alpha}a_{\alpha}}^{n0} + Y_{i_{\alpha}a_{\alpha}}^{m0} Y_{j_{\alpha}a_{\alpha}}^{n0} \right) \\
&+ \sum_{a_{\beta}} \left( X_{i_{\beta}a_{\beta}}^{m0} X_{j_{\beta}a_{\beta}}^{n0} + Y_{i_{\beta}a_{\beta}}^{m0} Y_{j_{\beta}a_{\beta}}^{n0} \right) \end{aligned}$$
(19)

$$\gamma_{ab,\text{unocc.}}^{mn} = -\sum_{i_{\alpha}} \left( X_{i_{\alpha}a_{\alpha}}^{m0} X_{i_{\alpha}b_{\alpha}}^{n0} + Y_{i_{\alpha}a_{\alpha}}^{m0} Y_{i_{\alpha}b_{\alpha}}^{n0} \right) - \sum_{i_{\beta}} \left( X_{i_{\beta}a_{\beta}}^{m0} X_{i_{\beta}b_{\beta}}^{n0} + Y_{i_{\beta}a_{\beta}}^{m0} Y_{i_{\beta}b_{\beta}}^{n0} \right)$$
(20)

The definition of the state-to-state 1-TDM is related to eq 10, where we have the trace of the product between the dipole moment matrix and the 1-TDM between two excited states. In this context, a TD-DFT state-to-state transition can be seen as the hole moving in the occ. space and the electron in the unocc. space. From the state-to-state 1-TDM, NTOs can be generated for both blocks.

The SF-sTD-DFT method<sup>34</sup> is defined in the collinear formulation of the spin-flip approach. As a result, the oneelectron TDM is defined by only the spin-flipping excitation coefficients as when assuming the Tamm–Dancoff approximation. Two types of NTOs could be defined. The first type describes spin-flip transitions from the triplet reference to the target spin-flip state where type-I SF-NTOs are generated from the SVD of the SF-1-TDM:

$$\gamma_{ia}^{m^{1 \text{or} 3} 0^{3}} = X_{i_{a} a_{\beta}}^{m^{1 \text{or} 3} 0^{3}} \tag{21}$$

where the target state could be a singlet or a low-spin triplet state ("1 or 3"). Note that type-1 SF-NTOs do not provide any real physical information; they just illustrate the spin-flip procedure, though they can be useful to interpret type-2 SF-NTOs. In the case in which the first SF state is a spin-pure ground state, the second type of NTOs concerns transitions from the first SF state to any SF states. Because the SF stateto-SF state transition dipole moment is defined in the SFsTD-DFT framework as

$$\langle m | \mu_{\xi} - \langle 0 | \mu_{\xi} | 0 \rangle | n \rangle_{\rm SF}$$

$$= \frac{\sqrt{2}}{2} \left[ \sum_{a_{\beta} i_{\alpha} j_{\alpha}} \left( X^{n}_{i_{\alpha} a_{\beta}} \mu_{i_{\alpha} j_{\alpha}, \xi} X^{m}_{j_{\alpha} a_{\beta}} \right) - \sum_{a_{\beta} b_{\beta} i_{\alpha}} \left( X^{n}_{i_{\alpha} a_{\beta}} \mu_{a_{\beta} b_{\beta}, \xi} X^{m}_{b_{\beta} i_{\alpha}} \right) \right]$$
(22)

Figure 5. Type-I NTOs for the SF transition from the triplet reference to the first SF state of 2,5-dimethylidenethiophene.



Figure 6. Type-II NTOs for the transition between the first (ground) and the second SF states of 2,5-dimethylidenethiophene.

the 1-TDM is composed of the occ. and unocc. blocks:

$$\boldsymbol{\gamma}_{\rm SF}^{mn} = \begin{pmatrix} \boldsymbol{\gamma}_{\rm occ.}^{mn} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{\gamma}_{\rm unocc.}^{mn} \end{pmatrix}$$
(23)

where

$$\gamma_{ji,\text{occ.}}^{mn} = \langle m | j_{\alpha}^{+} i_{\alpha} | n \rangle = \sum_{a_{\beta}} \left( X_{i_{\alpha}a_{\beta}}^{n} X_{j_{\alpha}a_{\beta}}^{m} \right)$$
(24)

and

$$\gamma_{ba,\text{unocc.}}^{mn} = \langle m | b_{\beta}^{+} a_{\beta} | n \rangle = -\sum_{i_{\alpha}} \left( X_{i_{\alpha} a_{\beta}}^{n} X_{b_{\beta} i_{\alpha}}^{m} \right)$$
(25)

In the same way as for state-to-state transitions, the 1-TDM diagonalization generates two block of type-II SF-NTOs. For a transition, the hole is moving in the  $\alpha$  occ. space and the electron in the  $\beta$  unocc. space, restraining quite drastically the singly excited space. The participation ratio is defined as

$$PR_{NTO}^{SF} = \frac{\left(\sum_{i} \lambda_{i,occ.} + \sum_{a} \lambda_{a,unocc.}\right)^{2}}{\sum_{i} \lambda_{i,occ.}^{2} + \sum_{a} \lambda_{a,unocc.}^{2}}$$
(26)

Figure 5 shows two pairs of type-I NTOs describing the spin-flip transition from the triplet reference to the first SF state of 2,5-dimethylidenethiophene. In the high-spin triplet state, both  $\alpha$  "quinoid" and "aromatic" MOs are filled while  $\beta$ MOs are empty. With a weight of 0.970, the first pair of NTOs shows that an electron moves from the  $\alpha$  "aromatic" NTO to the  $\beta$  "quinoid" NTO, resulting in a closed-shell configuration. The second transition with a small weight of 0.024 shows the reverse transition leading to a doubly excited determinant where both "aromatic" NTOs are filled. Thus, we have a  ${}^{1}\Psi_{E}$  type of state with a very small diradical character of 0.14 unpaired electron. Figure 6 shows type-II SF-NTOs for the transition between the first and second SF states. Two transitions are moving one electron from the "quinoid" to the "aromatic" NTOs in both occ. and unocc. spaces. This results in a  ${}^{1}\Psi_{D}$  type of state with 1.99 unpaired electrons. This straightforward description shows already the capability of SF-NTOs to describe such types of states. Note that NTOs are quite different from MOs because they encompass relaxation effects from the TD-DFT procedure and the compactness from the SVD or diagonalization operation.

# **III. COMPUTATIONAL DETAILS**

Natural transition orbitals are implemented in the sTDA program<sup>35</sup> for all methods available, including sTD-DFT and SF-sTD-DFT. Geometries of the first set of molecules were optimized with the GFN2-xTB method.<sup>55</sup> For the second set, their geometries were optimized with the GFN2-xTB method considering a closed-shell ground state and at the SF-B5050LYP/cc-pVDZ level for the first spin-flip state. Because we tried a higher-level optimization for spin-flip calculations in this second set, it seems fair to include them instead of their semiempirical counterparts, even if their geometries are almost identical. We deliberately selected a semiempirical method to optimize geometries to show the capability of new "low-cost" quantum chemistry methods. All absorption spectra were computed at the sTD-DFT and SF-sTD-DFT levels of theory with the M06-2X exchange correlation functional and the ccpVDZ basis set. For these two sets of molecules, M06-2X provides better spectral shapes than B5050LYP. To crudely estimate vibronic effects for molecule 27, a molecular dynamics (MD) simulation was carried out for 100 ps to equilibrate the system. Subsequently, a production run was conducted for 1000 ps. For both runs, using 298 K as the temperature, a time step of 4 fs was applied while constraining all bonds using the SHAKE algorithm. From the resulting trajectory, 200 snapshots were taken equidistantly and considered as input structures for the M06-2X/cc-pVDZ single-point calculations.

GFN2-xTB optimizations were performed with the xTB program.<sup>55</sup> All SCF calculations and SF-TD-DFT optimizations were performed with the Q-Chem  $5.1^{56}$  quantum chemistry package. The sTD-DFT and SF-sTD-DFT calculations were computed by sTDA.<sup>35</sup> All excitations up to 7 eV were computed for all absorption spectra with sTDA. To model the absorption spectra, transition strengths were broadened by Gaussians with a half-width at a 1/e maximum of 0.2 eV to best reproduce the experimental absorption bands. All NTOs are displayed considering an isovalue of 0.04.

# **IV. RESULTS**

At a finite temperature (typically the temperature of the experiment), the excited states of a molecule are populated according to a Boltzmann distribution. In diradicals, considering the small energy difference between SOMOs, it is *a priori* quite difficult to determine which state is the most populated. Figure 7 presents the comparison between



Figure 7. Experimental absorption spectra for the first set of compounds  $(11i, 20a, 21a, 22a, and 23a)^{18}$  compared to sTD-DFT and SF-sTD-DFT/M06-2X/cc-pVDZ calculations. Note that only 21a is in a high-spin triplet state. Systematic shifts of 0.6 and -0.2 eV were applied for both methods. The bottom right panel shows the comparison of the first absorption band among the set.

experimental and theoretical absorption spectra for the first set of molecules. As stated by Haley and co-workers<sup>18</sup> on the present compounds, "we did not set out to prepare biradical species, as a majority of the" Yamaguchi's "diradical character values of our molecules are less than 0.3". Using the approximate definition of Head-Gordon's diradical character (eq 8), **11i**, **20a**, **22a**, and **23a** have around 0.02 unpaired electron at the SF-sTD-DFT level for the singlet ground state. Then, it could be expected that a restricted scheme is already sufficient. We decided to treat these four compounds with both closed-shell and spin-flip sTD-DFT methods. Note that to best reproduce the experiment, we shifted excitation energies systematically for both methods: 0.6 eV for the restricted scheme and -0.2 eV for the SF one. We selected



Figure 8. Natural transition orbitals for the excitation from the ground state to the second excited state of 11i, 20a, 22a, and 23a obtained at the sTD-DFT level of theory.

both values to first match the first experimental band of 11i with computed ones. These two distinct values are due to differences in parametrizations. For 11i, the experimental spectrum is already well reproduced by the closed-shell sTD-DFT calculation. The energy difference between the two excited states with the largest oscillator strengths (2.20 eV) seems overestimated with respect to that from the experiment (1.46 eV). The same observation can be made for 20a, 22a, and 23a with values of 2.19 eV (exp 1.636 eV), 1.81 eV (1.29 eV), and 2.01 eV (1.33 eV), respectively. As already stated in our article about the SF-sTD-DFT method,<sup>34</sup> only low-lying excited states formed inside the spin-flip active space are described well by this level of theory. This is due to the large truncation of the CI space only allowing configuration state functions formed by the hole moving into the occ.  $\alpha$  space and the electron into the unocc.  $\beta$  space. As expected, the SFsTD-DFT method cannot reproduce higher-energy experimental peaks for 11i, 20a, 22a, and 23a but it added for each of them a small absorption peak just next to the lowest-energy peak. For 11i, it is not obvious that the extra peak is linked to the first peak higher-energy shoulder; for the three others, they seem to be related, at least regarding their intensities and spectral shapes. However, the energy differences between the first and second peaks are largely overestimated with respect to experiment: 11i (SF, 0.72 eV; exp, 0.17 eV), 20a (0.50 eV; 0.15 eV), 22a (0.36 eV; 0.17 eV), and 23a (0.39 eV; 0.16 eV). These large discrepancies are easily explained by looking at the nature of states. They are formed by several transitions in the occ.  $\alpha$  space from lower-energy MOs to the hole MO. They are all multiconfigurational states out of the SF active space. Thus, these spurious states should be spin-contaminated. Note that the evaluation of the spin contamination is not implemented in sTDA. Even so, without these SF results, the interpretation of the peak shoulder would be left to some possible vibronic couplings, but we show here that there is a possibility that this is actually due to another transition. Considering now 21a that we left over in the beginning of this section, only the high-spin triplet spectrum could reproduce the observed low-intensity band. Thus, considering this first set of molecules, only 21a is actually in a diradical state at room temperature while others are more in closed-shell singlet

states. The last panel of Figure 7 compares experimental to theoretical first absorption bands among this set of compounds. Trends are reproduced well, except for an energy inversion between 20a and 22a. Experimentally, maxima of absorption for 20a and 22a are located at 2.27 and 2.15 eV, respectively. We calculated an excitation energy (unshifted) for the transition from the ground state to the second excited state of 20a as 1.54 eV and of 22a as 1.64 eV. While reversed, both energy differences are on the same order of magnitude. Figure 8 presents the natural transition orbitals for the excitation to the second excited state of 11i, 20a, 22a, and 23a that correspond to the first absorption band of their respective spectra. For each of them, only one pair of NTOs is contributing to the excitation and represents the transition from the "quinoid" hole NTO to the "aromatic" electron NTO. The difference in excitation energies among these four compounds can be rationalized in terms of delocalization of their NTOs. With respect to 11i, 20a, and 22a, structures have been extended by adding a phenyl ring to both sides of the molecule but with a different arrangement/symmetry. While both have an extended  $\pi$ -conjugated pathway with respect to 11i, 20a presents more delocalized NTOs than 22a. This is due to symmetry constraints. It explains why we have computed a lower excitation energy for 20a. This clear and simple explanation does not clarify the reverse tendency observed experimentally. One possible explanation could be that experimental plots have been interchanged inadvertently, but this is only conjecture. The 23a transition is further stabilized by delocalization because of the two extra rings added. Finally, Figure 9 presents the NTOs for the transition to the third excited state of 21a that corresponds to the first absorption band of its high-spin triplet state. There, we have the transition from a lower-energy hole  $\beta$  NTO to the "quinoid" one.

Figure 10 shows the comparison of experimental spectra for the second set of compounds with respect to closed-shell and spin-flip sTD-DFT calculations. sTD-DFT energies remain shifted by 0.6 eV, while SF-sTD-DFT energies are not. These three [2,1-c]diindeno[n]thiophene derivatives (n = 1-3) also have very small diradical indices: 0.002 (27), 0.009 (28), and 0.026 (29) unpaired electron. Like for the previous set, we



Figure 9. Natural transition orbitals describing the transition from its high-spin triplet ground state to the third excited state of 21a obtained at the UsTD-DFT level of theory.

used both closed-shell and spin-flip sTD-DFT methods. In this context, the SF method improves here the description of low-lying excited states. The three spectra display two absorption bands that are already well reproduced by restricted calculations. However, the SF-sTD-DFT method seems to better reproduce energy differences between the two main bands. This can be rationalized by looking to the NTOs. For 27, the first panel of Figure 11 presents the pair of type-I NTOs generated by the SF procedure, going from the highspin triplet reference to the first SF state (here the closed-shell ground state), emptying the "aromatic" NTO to fill the "quinoid" one. The second panel of Figure 11 presents type-II NTOs for the transition from the first SF state to the third one that corresponds to the first absorption band of 27. The first pair of NTOs with a weight of 0.564 shows the transition from a "quinoid" NTO, including some compactness/ relaxation effects to the "aromatic" one. The hole NTO is a weighted superposition of two contiguous  $\alpha$  spin-orbitals. This first pair of NTOs is also present as a unique pair of NTOs in the closed-shell calculation. The second pair shows the same transition but in the  $\beta$  unocc. space with a slightly lower weight of 0.397. Thus, it could not include the same compactness/relaxation effect. Hence, this transition is probably better described by the closed-shell calculation. The third panel of Figure 11 presents the transition from the first SF state to the fifth one that corresponds to the second absorption band. This transition has two pairs of type-II NTOs contributing. The first one has a large weight of 0.856 and shows the transition from the  $\alpha$  orbital just below in energy the "quinoid" one to the "aromatic" NTO. Even if this is not obvious looking when looking at the pictures, the present hole NTO is the same orbital that adds a compactness/relaxation effect to the hole NTO from the

first pair that descibes the transition from the first SF state to the third. As this type of hole NTO is also important for the two other molecules, we propose to call it the " $\pi$ -bonded" NTO because it has one  $\pi$ -orbital in the thiophene cycle and two  $\pi$ -orbitals in both phenyl rings. Note that this terminology does not imply that this is the only orbital presenting  $\pi$ -bonds. It is used to ease the following discussions. The low-weight second pair shows the transition from the "quinoid" NTO to the "aromatic" NTO. This second contribution is also present in the closed-shell calculation but with a smaller weight. This actually explains the difference between both theoretical spectra. Because nuclear gradients are not implemented at the sTD-DFT level, we cannot estimate vibronic couplings. A crude way to estimate this is to run a molecular dynamics simulation and compute absorption spectra for several snapshots. Figure 12 shows the comparison of the so-obtained spectrum with experiment. As expected for such a rigid system, the vibronic couplings are qualitatively described but underestimated. However, it gives an idea how the coupling impacts the first peak broadening and the second peak splitting.

The first panel of Figure 13 presents type-I NTOs that describe the generation of the first SF state from the triplet reference of 28. Here as for the previous case, the first pair of NTOs with a weight of 0.971 shows the SF transition from the  $\alpha$  "aromatic" NTO to the  $\beta$  "quinoid" one, resulting in a closed-shell configuration. In addition, a low-weight second pair of type-I NTOs also contributes to the first SF state, leading to a doubly excited configuration. This explains the slightly higher diradical index observed for 28 than for 27. The second panel of Figure 13 displays the transition from the first SF state to the fourth one that corresponds to the first absorption band. This transition is very similar to that from 27. It is also an open-shell singlet state obtained by the transition from the "quinoid" NTO to the "aromatic" one in both spin spaces. The hole NTO in the  $\alpha$  space includes some compactness/relaxation effects due to the superposition with a small contribution from the " $\pi$ -bonded" orbital, as we observed for 27. The electron NTO from the second pair also shows some compactness/relaxation effects that are difficult to assign. Note that for the closed-shell result with respect to the SF one, the discussion is similar to that for 27. For the second absorption band, the third panel of Figure 13 shows the transition from the first SF state to the fifth one. The highest-weight pair of NTOs presents the transition from



Figure 10. Experimental absorption spectra for the second set of compounds  $(27-29)^{18}$  compared to sTD-DFT and SF-sTD-DFT/M06-2X/ccpVDZ calculations. A systematic shifts of 0.6 eV was applied at the sTD-DFT level of theory.



Figure 11. Selected NTOs of 27.



Figure 12. Comparison of experimental and theoretical (SF-sTD-DFT/M06-2X/cc-pVDZ) absorption spectra. The theoretical data were obtained by averaging our 200 snapshots from an MD simulation to account for vibronic effects.

the " $\pi$ -bonded" NTO to the "aromatic" one. The second pair with a low weight of 0.109 displays the transition from "quinoid" to "aromatic" NTOs. In the closed-shell calculation, this second contribution has a lower weight with respect to the SF result. As for 27, this is probably why the SF spectrum better reproduces the experimental one. With respect to 27's spectra, energy shifts due to increasing the level of delocalization seem negligible. However, for the first band, the observed higher intensity for 28 is possibly due to the change in symmetry from  $C_{2\nu}$  for 27 to  $C_{2h}$ . B<sub>u</sub> states in  $C_{2h}$ are dipole-allowed for both x and y polarizations, while B<sub>1</sub> and  $B_2$  in  $C_{2v}$  are for only *x* and *y*, respectively. This is in contradiction with the statement of Haley and co-workers<sup>18</sup> about the presence of an inversion center that we recall in the Introduction.

The case of 29 is a bit different from the two previous ones. The largest conjugation pathway seems to stabilize more the "quinoid" orbital rather than the " $\pi$ -bonded" one. Thus, the "quinoid" MO is already doubly occupied. In this context, the SF procedure empties the "aromatic"  $\alpha$  NTO to fill the " $\pi$ bonded"  $\beta$  NTO (see the first panel of Figure 14). In addition, a low-weight pair of NTOs that forms a doubly excited configuration also contributes to the first SF state. The transition from the first SF state to the third one that corresponds to the first absorption band is presented in the second panel of Figure 14. Two pairs of NTOs are contributing to this transition. The first one shows a transition from the hole NTO that corresponds to a weighted superposition of the " $\pi$ -bonded" and "quinoid" orbitals to the "aromatic" one. The second pair presents a lower weight of 0.212 showing the same transition but without compactness/relaxation effects because the "quinoid"  $\beta$  MO is not included in the unocc.  $\beta$  space. The SF method seems to provide a better intensity for this transition than the closedshell method, or it is the relative intensity of the second peak that is better described. The second observed transition is described at the SF-sTD-DFT level by type-II NTOs shown in the third panel of Figure 14. With a  $\lambda$  of 0.623, the first pair of NTO shows a transition from "quinoid" to "aromatic" NTOs. The second lower-weight configuration is obtained by exciting an electron from " $\pi$ -bonded" to "aromatic" NTOs. With



Figure 13. Selected NTOs of 28.





respect to 27 and 28, spectra are red-shifted due to delocalization effects.

For all compounds with the exception of **21a**, Figure 15 compares experimental maxima of absorption for the first visible transition to theoretical values at both sTD-DFT and SF-sTD-DFT levels of theory. As suggested above, experimental values of **20a** and **22a** were interchanged. Note that the theoretical values are not shifted. Both sets of data were linearly fitted. With an  $R^2$  of 0.9604, the SF-sTD-DFT values present the best linear relation with respect to the experiment, because of the amount of static correlation recovered by the spin-flip active space. However, a systematic overestimation is observed, probably due to missing solvent effects, the choice of the XC functional, and the truncated active space.

# **V. CONCLUSIONS**

Considering all indenofluorene derivatives from this study, only 21 is a high-spin triplet diradical. All other molecules are singlet  ${}^{1}\Psi_{\rm E}$  type states with a very small contribution from a doubly excited configuration, resulting in low diradical characters. While these systems could be regarded as closedshell systems, the multiconfigurational treatment provided by the SF active space improves the description of the low-lying excited states. For the first set of molecules, it was able to recover information about the origin of the shoulder of the first absorption bands. Considering the second set, it improves relative excitation energies and intensities. The implementation of NTOs in the sTDA program provides a powerful way to interpret absorption spectra at simplified levels. Consider-



**Figure 15.** Theoretical first visible excitation energy as a function of the experimental excitation energy at both sTD-DFT and SF-sTD-DFT levels of theory and respective linear fits. Note that the experimental values of **20a** and **22a** are interchanged.

ing the three types of most relevant orbitals that we defined for these systems, i.e., "quinoid", "aromatic", and " $\pi$ -bonded", we provided a very simple interpretation of the low-lying excited states resulting from their excitations. From a methodological point of view, the SF-sTD-DFT procedure successfully described the absorption spectra of all systems, efficiently.

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### Notes

The authors declare no competing financial interest.

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