Effect of the diradical character on static polarizabilities and two-photon absorption cross sections: A closer look with spin-flip equation-of-motion coupled-cluster singles and doubles method

Kaushik D. Nanda and Anna I. Krylov
Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482, USA

(Received 29 March 2017; accepted 19 May 2017; published online 12 June 2017)

We present static polarizabilities and two-photon absorption (2PA) cross sections for the low-lying electronic states of prototypical diradicals such as benzenes and analogues of m-xylylene and p-quinodimethane computed with the spin-flip equation-of-motion coupled-cluster singles and doubles (EOM-SF-CCSD) method. The static polarizabilities were calculated as analytic second derivatives of the EOM energies, and the 2PA cross sections were calculated using the expectation-value approach. We explain the trends in the nonlinear responses of the SF target states by constructing few-states models based on truncated sum-over-states expressions for these nonlinear properties. By using a Hückel-type treatment of the frontier molecular orbitals that host the unpaired electrons, we rationalize the trends in the dipole interactions between the SF target states relevant in the few-states models. We demonstrate the correlation between the nonlinear responses of these electronic states and the diradical character. Published by AIP Publishing.

I. INTRODUCTION

Organic molecules with tunable nonlinear response properties such as two-photon absorption (2PA) cross sections and (hyper)polarizabilities serve as building blocks for materials used in nonlinear optics. For example, organic chromophores with large and tunable 2PA cross sections are exploited in applications such as photodynamic cancer therapy, molecular switches in optogenetics, bioimaging, optical limiting, and three-dimensional optical data storage.1–9 Macroscopic properties such as the dielectric constant and refractive index of a substance are related to the molecular static polarizability via the Clausius-Mossotti and Lorentz-Lorenz equations, respectively.10,11 Static polarizability can also be used as a descriptor of molecular conductance in molecular junctions.12 While the bulk of nonlinear materials has utilized closed-shell systems, a novel design strategy based on open-shell systems such as diradicals and polycyclic aromatic hydrocarbons (PAHs) with open-shell ground states has been explored recently,13–21 motivated by theoretical predictions that open-shell systems have larger nonlinear responses relative to their closed-shell counterparts. Another example of utilizing open-shell states to enhance nonlinear responses was proposed by Marks and Ratner, who have considered twisted π-system chromophores featuring increased diradical character.22–26 Here, we investigate nonlinear responses of open-shell systems using a state-of-the-art electronic structure method, aiming to gain a molecular-level understanding of 2PA cross sections and static polarizabilities in prototypical diradicals.

The design of novel nonlinear materials requires establishing structure-property relationships, which can be facilitated by calculations using reliable theoretical methods. By being able to simulate the experimental observables such as 2PA spectra, theoretical methods can also help in interpreting experimental results.27,28 The ability of theoretical methods to accurately calculate the response properties is thus critical for connecting the molecular structure to the experimental observable. In addition to the accurate calculations of the properties, analysis tools for interpreting computed properties are crucial for establishing design principles. In this paper, we demonstrate how such interpretation tools can help explain the trends in the calculated response properties of diradicals.

It is well established that computed nonlinear properties are sensitive to the details of underlying electronic structure methods. For example, using large basis sets with additional diffuse functions and correlated methods is essential for accurate calculations of nonlinear properties in some systems.29–31 In the case of diradicals, the ability to accurately describe multiconfigurational wave functions becomes an additional prerequisite. The standard wave-function methods based on a single Slater determinant are not sufficient for these purposes. The spin-flip equation-of-motion coupled-cluster singles and doubles (EOM-SF-CCSD) method31–33 provides an efficient single-reference strategy for a balanced treatment of the static and dynamical electron correlation essential for the accurate description of the multiconfigurational wave functions in systems such as diradicals and triradicals. This method and its variants, i.e., spin-flip time-dependent density functional theory34–39 (SF-TDDFT) and restricted active space spin-flip configuration interaction40,41 (RASSF-CI), have been used to model a variety of strongly correlated systems.31,32,34,39,41–51 Finite-field calculations for static second hyperpolarizabilities with energies from SF configuration interaction (SF-CI) methods have also been reported.52 However, nonlinear properties such as static polarizabilities and 2PA cross sections have not been investigated with the EOM-SF-CCSD method prior to Ref. 53 and this work.

0021-9606/2017/146(22)/224103/16/$30.00 146, 224103-1 Published by AIP Publishing.
The exact mathematical expressions for these nonlinear response properties (e.g., the sum-over-states expressions for 2PA transition moments and polarizabilities) imply that their accurate calculations require an accurate description of the full spectrum of eigenstates including their energies and dipole couplings. Thus, it is important to quantify the effect of static correlation on these response properties. We recently discussed the effects of correlation on static polarizabilities by comparing the EOM-EE-CCSD and EOM-SF-CCSD results for methylene and $p$-benzene. While the EOM-SF-CCSD results agreed well with the results from an earlier study employing a multireference coupled-cluster method, we found that the poor description of the multi-configurational states with EOM-EE-CCSD had a significant effect on not only the static polarizabilities of these states but also of the states that are well described by the EOM-EE-CCSD ansatz, but are dipole-coupled to these poorly described states.

Nakano and co-workers, who pioneered the idea of using open-shell motifs in designing nonlinear materials, have studied response properties such as 2PA cross sections and (hyper)polarizabilities of few open-shell diradical systems using a variety of DFT, perturbation theory, and coupled-cluster methods. These studies have established a correlation between these properties and the diradical character (a theoretically defined quantity). In particular, Nakano and co-workers have reported a bell-shape dependence of second hyperpolarizability of the singlet ground state in quinodimethane on the diradical character imparted by the resonance between its quinoid and benzenoid forms and suggested that it is an intermediate diradical character that gives rise to the largest nonlinear response. On the basis of this observation, these authors proposed designs based on PAHs that show enhanced second hyperpolarizabilities. A combined experimental-theoretical study of similar PAHs has established a correlation between their large 2PA cross sections and diradical character. In this paper, we extend these studies by investigating the response of low-lying electronically excited states that have not been characterized before. By employing an electronic structure approach capable of describing the non-dynamical correlation and multiconfigurational wave functions, we validate the main findings of prior theoretical work.

The EOM-SF-CCSD method has been used to characterize the structures and electronic states of prototypical diradicals. Here, we calculate the EOM-SF-CCSD static polarizabilities and 2PA cross sections of low-lying electronic states in benzenes, $m$-didehydroxylylenes, $p$-quinodimethane (PQM), and extended PQM (Chichibabin analogue). We analyze the results by constructing truncated sum-over-states models for these response properties. Consistent with the previous studies, we find a correlation between the nonlinear response and the diradical character. An approximate measure of the diradical character is given by the ratios of leading wave function amplitudes. More rigorously, the diradical character can be quantified by calculating Head-Gordon’s index, which is orbital-invariant and can be computed for any wave function. Our results demonstrate that structure-property relationships for these response properties in diradicals can be established on the basis of the diradical character, distance between the radical centers, and energy gaps.

The paper is organized as follows. Section II A presents the spin-flip methods for diradicals and explains why this method gives a balanced description of the static and dynamical correlation effects in multiconfigurational wave functions. Sections II B and II C present the formalism for calculating static polarizability and 2PA cross sections within the EOM-SF-CCSD framework. Section II D derives approximate expressions for the transition dipole moments between the low-lying electronic states of diradicals in terms of the diradical character. In Sec. II E, we relate Head-Gordon’s index to an approximate parameter for the diradical character in a simple two-electrons-in-two-molecular-orbitals case. Section III gives the computational details. Section IV presents the results for static polarizabilities and 2PA cross sections for selected diradicals, analyzes the dependence of these properties on the diradical character, and explains the observed trends using few-states models.

II. THEORY

A. EOM-SF-CCSD method for diradicals

A diradical is a system with two electrons in two nearly degenerate molecular orbitals (MOs). Two electrons in two MOs ($\phi_1$ and $\phi_2$) gives rise to the six Slater determinants shown in Fig. 1. The high-spin ($M_s = 1$) determinants, (a) and (b), and the closed-shell determinants, (e) and (f), are eigenfunctions of $\hat{S}^2$, whereas the low-spin ($M_s = 0$) open-shell determinants (c) and (d) are not. Wave functions, which are eigenfunctions of $\hat{S}^2$, can be constructed by taking linear combinations of these determinants. The determinants (e) and (f) correspond to totally symmetric configurations; these form the closed-shell singlet (CSS1) states (E) and (F) in Fig. 1. Here, $\lambda$ is an indicator of the diradical character and depends on the energy separation of the two MOs. When the two MOs are degenerate, $\lambda = 1$. Determinants (a) and (b) describe the high-spin ($M_s = \pm 1$) triplet states (A) and (B), respectively. The low-spin ($M_s = 0$) triplet wave function (C) and the open-shell singlet (OSS) wave function (D) in Fig. 1 are the linear combinations of determinants (c) and (d). The configurations from Fig. 1 form the manifold of diradical states (which we will refer to as the primary diradical manifold):

$$3\Psi_A = \frac{1}{\sqrt{2}} (\phi_1 \phi_2 - \phi_2 \phi_1) (\alpha \alpha), \quad \text{(1)}$$

FIG. 1. Top row: Six Slater determinants obtained by distributing two unpaired electrons in two nearly degenerate molecular orbitals. Bottom row: Linear combinations of these determinants gives rise to six diradical wave functions that are eigenfunctions of $\hat{S}^2$. 

\[3\psi_B = \frac{1}{\sqrt{2}} (\phi_1 \phi_2 - \phi_2 \phi_1) (\beta \beta),\]
\[3\psi_C = \frac{1}{2} (\phi_1 \phi_2 - \phi_2 \phi_1) (\alpha \beta + \beta \alpha),\]
\[1\psi_D = \frac{1}{2} (\phi_1 \phi_2 + \phi_2 \phi_1) (\alpha \beta - \beta \alpha),\]
\[1\psi_E = \frac{1}{2 \sqrt{1 + \lambda^2}} \left( (\phi_1)^2 - \lambda (\phi_2)^2 \right) (\alpha \beta - \beta \alpha),\]
\[1\psi_F = \frac{1}{2 \sqrt{1 + \lambda^2}} \left( \lambda (\phi_1)^2 + (\phi_2)^2 \right) (\alpha \beta - \beta \alpha).\]

Here, the spatial parts of these wave functions are denoted by linear combinations of \(\phi_i \phi_j\) [stands for \(\phi_i(r_1) \phi_j(r_2)\) for electrons 1 and 2]. The spin parts are denoted by linear combinations of the products of spin functions \(\alpha\) and \(\beta\) [\(\alpha \beta\) stands for \(\alpha(1) \beta(2)\)]. The wave functions (C)-(F) are all multiconfigurational. Therefore, they are not well described by methods such as CCSD, which gives preference for one configuration over another. However, these states can be accurately described in a single-reference framework by EOM-SF-CCSD.

In the EOM-CC method for excitation energies (EOM-EE),\(^\text{60-66}\) the target wave functions are generated by the EOM operator \(R_{M_\alpha=0}\) connecting, in the Fock space, the reference state \(\psi^0\) and the target state as follows:
\[\lambda \psi_{M_\alpha=0} = R_{M_\alpha=0} \psi_{M_\alpha=0}.\]

When the closed-shell reference state \((\lambda \approx 0)\) can be accurately described using a single-reference wave function, the singlet or triplet excited states obtained with the above parameterization are also well described. However, the closed-shell diradical wave functions, (E) and (F), are multiconfigurational, which renders the above parameterization of the excited states inappropriate. In particular, the wave function (F) may have significant contribution from determinant (f), which cannot be obtained by a single excitation from the single-reference closed-shell state, unlike determinants (c) and (d). Although double excitations are included in the EOM-EE-CCSD ansatz, the description of the state (F) is poor owing to an unbalanced treatment of the two leading determinants.

The SF method exploits the fact that the determinants (c)-(f) can all be obtained by the single spin-flip excitation of high-spin state (A) or (B), which can be well described by a single-reference ansatz (we note that both dynamical and static correlations are smaller for high-spin states\(^\text{32}\)). The target SF wave functions are parameterized as follows:
\[\lambda \psi_{M_\alpha=0} = R_{M_\alpha=0} \psi_{M_\alpha=0}.\]

This enables a single-reference treatment of all the multiconfigurational states within the SF framework. In EOM-SF-CCSD, the reference state is a high-spin CCSD reference state and the EOM operator \(R_{M_\alpha=1}\) includes single and double excitations with a single spin-flip. Note that the SF method provides spin-pure wave functions only when the SF active space is restricted to two electrons in two MOs. In practice, while the SF target states are spin-incomplete, spin contamination is small for the states from the primary diradical manifold (i.e., those shown in Fig. 1). Several approaches have been developed in order to minimize or eliminate spin contamination in the SF methods\(^\text{67-74}\) Here we use the original, non-spin-adapted version\(^\text{31,32}\) of EOM-SF-CC.

### B. Static polarizabilities with EOM-SF-CCSD

The dipole polarizability of a system is defined as the linear response of its dipole moment in the presence of an external electric field. In the static limit, the polarizability components for \(k\)th electronic state are given by the second derivative of its energy \(E_k\) with respect to the two electric-field perturbations,\(^\text{75}\)
\[\alpha^k_{xy} = -\frac{\delta^2 E_k}{\delta E_x \delta E_y}.\]

For exact state \(\Psi_k\), the dipole polarizability is given by the following sum-over-states expression:\(^\text{76,77}\)
\[\alpha^k_{xy}(\omega, -\omega) = \sum_{n \neq k} \left( \frac{\langle \Psi_k | \mu_x | \Psi_n \rangle \langle \Psi_n | \mu_y | \Psi_k \rangle}{E_n - E_k - \omega} + \frac{\langle \Psi_k | \mu_y | \Psi_n \rangle \langle \Psi_n | \mu_x | \Psi_k \rangle}{E_n - E_k + \omega} \right).\]

Here, \(\mu_x\) is the \(x\)-component of the dipole moment operator of the system which interacts with the electric-field perturbation with frequency \(\omega\). The sum runs over all electronic states except \(\Psi_k\). Expressions (9) and (10) are equivalent for exact states. For approximate EOM-XX-CCSD states, these two expressions give different results.

Our analytic-derivative implementation\(^\text{53}\) is based on Eq. (9) and is formulated using the EOM energy Lagrangian and its second derivatives with respect to the electric-field perturbations (orbital relaxation is omitted). An alternative expectation-value approach to calculating polarizabilities involves using EOM-CCSD energies and transition moments in Eq. (10). The sum-over-states expression is converted into a computationally tractable form by using the resolvent expression and then introducing response vectors to give a formulation that is formally and numerically identical to the sum-over-states expression. In Ref. 53, we showed that for the EOM states, polarizabilities computed with these two formulations could differ as much as by 30\%. Here, we only employ the analytic-derivative approach for calculating static polarizabilities.

### C. 2PA cross sections with EOM-SF-CCSD

The right and left 2PA transition moments between the exact states \(\Psi_i\) and \(\Psi_f\) are given by the following sum-over-states expressions:
\[M^i_{xf} = -\sum_n \left( \frac{\langle \Psi_i | \mu_x | \Psi_n \rangle \langle \Psi_n | \mu_y | \Psi_f \rangle}{\Omega_{ni} - \omega_x} + \frac{\langle \Psi_i | \mu_y | \Psi_n \rangle \langle \Psi_n | \mu_x | \Psi_f \rangle}{\Omega_{ni} - \omega_y} \right),\]
\[M^f_{xy} = -\sum_n \left( \frac{\langle \Psi_f | \mu_x | \Psi_n \rangle \langle \Psi_n | \mu_y | \Psi_i \rangle}{\Omega_{nf} - \omega_x} + \frac{\langle \Psi_f | \mu_y | \Psi_n \rangle \langle \Psi_n | \mu_x | \Psi_i \rangle}{\Omega_{nf} - \omega_y} \right),\]
where \(\Omega_{ni} = E_n - E_i\) and \(\omega_x\) and \(\omega_y\) are the frequencies of the two absorbed photons (polarized along the \(x\)- and \(y\)-direction) such that \(\omega_x + \omega_y = \Omega_f\). In this study, we only consider 2PA transitions with degenerate photons (\(\omega_x = \omega_y = \Omega\)). The sum runs over all electronic states of the system. The right and
left 2PA transition moments are different because of the non-Hermitian nature of EOM-CC theory. Our expectation-value EOM-CCSD implementation involves using EOM-CCSD energies and transition moments in Eqs. (11) and (12). Similar to the expectation-value approach for polarizabilities, the sum-over-states expression is converted into a computationally efficient form by using the resolvent expression and then introducing response vectors. This formulation is formally and numerically identical to the sum-over-states expression.

The microscopic 2PA cross section, $\sigma^{2PA}$, is given by the following equation:

$$
\sigma^{2PA} = \frac{F}{30} \sum_{a,b} S_{a,b} + \frac{G}{30} \sum_{a,b} S_{a,b} + \frac{H}{30} \sum_{a,b} S_{a,b},
$$

where the 2PA transition strength matrix elements $S_{ab,cd}$ are given by the product of the left and right 2PA transition moments as follows:

$$
S_{ab,cd}^{if} = \frac{1}{2} \left( M_{ab}^{f-r} (-\omega) M_{cd}^{r-i} (\omega) + M_{cd}^{r-f} (-\omega) M_{ab}^{f-i} (\omega) \right),
$$

$F, G,$ and $H$ are constants that depend on the polarization of the incident light. Here, we only consider the case of parallel linearly polarized light ($F = G = H = 2$). The macroscopic 2PA cross sections, $\sigma^{2PA}$ (in GM), are computed using $\delta^{2PA}$ according to the formula given in Ref. 78.

**D. Transition dipole moments between SF target states**

The sum-over-states expressions, Eqs. (10)–(12), can be approximated by several leading terms giving rise to the few-states models. While their convergence could be slow, such approximate few-states models help to rationalize the trends in the response properties. Here, we consider few-states models for the 2PA transition moments and static polarizabilities of the closed-shell and open-shell singlet states, which are based on the sum-over-states expressions and require the calculations of the transition energies and transition dipole moments. In this subsection, we evaluate the transition dipole moments between the SF states (D) and (E) and between the SF states (D) and (F). We employ the Hückel-type representation of the frontier MOs to further express these transition dipole moments in terms of the atomic orbitals (AOs).

First, we evaluate the transition moment between the states (D) and (E) as follows:

$$
\langle \Psi_D | \mu | \Psi_E \rangle = \frac{1}{2} \left( \phi_1 \phi_2 + \phi_2 \phi_1 \right) (\alpha \beta - \beta \alpha) |\mu| \frac{1}{2\sqrt{1 + \lambda^2}} \left( (\phi_1)^2 - \lambda (\phi_2)^2 \right) (\alpha \beta - \beta \alpha)
$$

$$
= \frac{1}{4 \sqrt{1 + \lambda^2}} \left( (\phi_1 \phi_2 + \phi_2 \phi_1) |\mu| (\phi_1)^2 - \lambda (\phi_2)^2 \right) = \frac{1}{4 \sqrt{1 + \lambda^2}} \left( (\phi_2 |\mu| \phi_1) - \lambda (\phi_1 |\mu| \phi_2) + (\phi_2 |\mu| \phi_1) - \lambda (\phi_1 |\mu| \phi_2) \right)
$$

$$
= \frac{1}{2 \sqrt{1 + \lambda^2}} (1 - \lambda) \langle \phi_1 |\mu| \phi_2 \rangle,
$$

where we use $\langle \phi_1 |\mu| \phi_2 \rangle = \langle \phi_2 |\mu| \phi_1 \rangle$ in the last step. When the frontier orbitals, $\phi_1$ and $\phi_2$, form a bonding-antibonding MO pair from two AOs, we have

$$
\phi_1 = \frac{1}{\sqrt{2}} (\chi_1 + \chi_2),
$$

$$
\phi_2 = \frac{1}{\sqrt{2}} (\chi_1 - \chi_2),
$$

where $\chi_1$ and $\chi_2$ are the AOs localized on the radical centers. The transition dipole moment is then given by

$$
\langle \Psi_D | \mu | \Psi_E \rangle = \frac{1}{2 \sqrt{1 + \lambda^2}} (1 - \lambda) \frac{1}{\sqrt{2}} (\chi_1 + \chi_2) |\mu| \frac{1}{\sqrt{2}} (\chi_1 - \chi_2)
$$

$$
\approx \frac{1}{4 \sqrt{1 + \lambda^2}} (1 - \lambda) \left( (\chi_1 |\mu| \chi_2) - (\chi_2 |\mu| \chi_1) \right)
$$

$$
\approx \frac{1}{4 \sqrt{1 + \lambda^2}} \left( (\chi_2 |\chi_1| \chi_2) - (\chi_1 |\chi_1| \chi_1) \right)
$$

$$
\approx \frac{1}{4 \sqrt{1 + \lambda^2}} \left( (\chi_2 |\chi_2| \chi_2) - (\chi_1 |\chi_1| \chi_1) \right)
$$

$$
\approx \frac{1}{4 \sqrt{1 + \lambda^2}} \left( (\chi_2 |\chi_2| \chi_2) - (\chi_1 |\chi_2| \chi_1) \right)
$$

$$
\approx \frac{1}{4 \sqrt{1 + \lambda^2}} \left( (\chi_2 |\chi_2| \chi_2) - (\chi_1 |\chi_1| \chi_1) \right)
$$

$$
= \frac{1}{4 \sqrt{1 + \lambda^2}} (1 + \lambda) R_{12},
$$

where $\langle \chi_1 |\chi_2 \rangle \approx X_1$ denotes the position of nucleus 1, $X_2 - X_1 = R_{12}$ denotes the distance between nuclei 1 and 2, and we assume that $\langle \chi_1 |\chi_2 \rangle = 0$ if $\chi_1$ and $\chi_2$ belong to different centers. Equation (18) implies that for a fixed $\lambda$, the transition dipole moment between wave functions (D) and (E) increases as the distance between the radical centers (on which the $\chi$s are located) increases. For a fixed distance between the radical centers, this transition dipole moment increases when $\lambda$ decreases ($\frac{1 + \lambda}{\sqrt{1 + \lambda^2}}$ is a decreasing function for $0 \leq \lambda \leq 1$). In other words, as the diradical character decreases, this transition dipole moment increases. This derivation (and the result) is similar to that from Ref. 15.

Similarly, the transition dipole moment between states (D) and (F) is given by

$$
\langle \Psi_D | \mu | \Psi_F \rangle = \frac{1}{2 \sqrt{1 + \lambda^2}} (1 + \lambda) \langle \phi_1 |\mu| \phi_2 \rangle,
$$

$$
\langle \Psi_D | \mu | \Psi_F \rangle \approx \frac{1}{4 \sqrt{1 + \lambda^2}} (1 + \lambda) \langle \chi_2 |\chi_2 \rangle - (\chi_1 |\chi_1| \chi_1) \rangle
$$

$$
\approx \frac{1}{4 \sqrt{1 + \lambda^2}} (1 + \lambda) R_{12}.
$$

This transition dipole moment increases for a fixed $\lambda$ when the distance between the radical centers increases and also when $\lambda$ increases for a fixed distance between the radical centers. Thus, Eqs. (18) and (20) connect the transition dipole moments between diradical states with the (i) distance between the centers hosting the unpaired electrons and (ii) diradical character.
E. Relationship between \( \lambda \) and Head-Gordon’s diradical index

We explain the trends in the relevant transition moments between different electronic states of the diradicals using an approximate measure of the diradical character, \( \lambda \). While \( \lambda \) provides an unambiguous measure of the diradical character for a system of two electrons in two MOs, it becomes less appropriate for more complex wave functions, which include configurations beyond those shown in Fig. 1.

A more rigorous way to quantify the diradical character is based on the density matrix.\(^7\) One can define the density matrix of effectively unpaired electrons, whose trace can be interpreted as the total number of unpaired electrons in the system. Several definitions of this index have been introduced.\(^{56,80,81}\) Here, we employ Head-Gordon’s index\(^{56}\) defined as

\[
n_u = \sum_i \bar{n}_i(2 - \bar{n}_i),
\]

where \( \bar{n}_i \) are the spin-averaged occupation numbers of the natural orbitals (eigenvectors of the state density matrix) and \( n_u \) is the number of effectively unpaired electrons. The utility of this index has been illustrated in several studies of systems with two or more unpaired electrons.\(^{79,82-84}\)

Here, we provide the relationship between \( n_u \) and \( \lambda \) for the simplistic diradical system of two electrons in two MOs (Fig. 1). \( \lambda \) can be computed using the ratio of the amplitudes of the configurations (f) and (e) in wave function (E) shown in Fig. 1 and given by Eq. (5).

We rewrite the expression for wave function (E) as follows:

\[
\Psi_E = \frac{1}{2} \left( \sqrt{1 - \Lambda^2} \phi_1^2 - \Lambda \phi_2^2 \right) (\alpha \beta - \beta \alpha),
\]

where \( \Lambda = \frac{\lambda}{\sqrt{\pi \omega}} \). The state density matrix, \( \gamma_{pq} \), is then given by

\[
\gamma_{pq} = \langle \Psi_E | \hat{a}_{p \dagger} \hat{a}_{q \dagger} | \Psi_E \rangle = \left( 1 - \Lambda^2 \right) \langle (\phi_1^2)^\dagger \hat{a}_{p \dagger} \hat{a}_{q \dagger} (\phi_1^2) \rangle
- \Lambda \sqrt{1 - \Lambda^2} \langle (\phi_1^2)^\dagger \hat{a}_{p \dagger} \hat{a}_{q \dagger} (\phi_2^2) \rangle + \Lambda^2 \langle (\phi_2^2)^\dagger \hat{a}_{p \dagger} \hat{a}_{q \dagger} (\phi_2^2) \rangle,
\]

where \( \hat{a}_{p \dagger} \) and \( \hat{a}_{q \dagger} \) are the creation and annihilation operators of an electron in spin orbitals \( p \) and \( q \), respectively (\( p \neq q \)). The state density matrix in the spin-orbital basis is diagonal and given by

\[
\gamma = \begin{pmatrix}
1 - \Lambda^2 & 0 & 0 & 0 \\
0 & 1 - \Lambda^2 & 0 & 0 \\
0 & 0 & \Lambda^2 & 0 \\
0 & 0 & 0 & \Lambda^2
\end{pmatrix}.
\]

This means that the MOs \( \phi_1 \) and \( \phi_2 \) are also the natural orbitals for this system with spin-averaged occupation numbers, \( \bar{n}_1 = 2 - 2\Lambda^2 \) and \( \bar{n}_2 = 2\Lambda^2 \). The Head-Gordon index is then

\[
n_u = 2(2\Lambda^2)^2 \left( 2 - 2\Lambda^2 \right)^2 = 32 \Lambda^4 \left( 1 - \Lambda^2 \right)^2 = \frac{32 \lambda^4}{(1 + \lambda^2)^4}.
\]

This relationship between \( n_u \) and \( \lambda \) can be easily verified by a calculation of a two-electrons-in-two-MOs system such as the hydrogen molecule in the minimal basis set (presented in supplementary material).

III. COMPUTATIONAL DETAILS

We computed static polarizabilities and 2PA cross sections with the EOM-SF-CCSD method and the Dunning aug-cc-pVDZ basis set using the Q-Chem quantum chemistry package.\(^{85,86}\) The unrestricted Hartree-Fock (UHF) high-spin reference states were used in the calculations of benzenes. The restricted open-shell Hartree-Fock (ROHF) high-spin references were used for \( m \)-didehydro-xylylenes, PQM, and Chichibabin analogue to mitigate the spin contamination in the reference [e.g., the UHF high-spin reference of \( m \)-xylylene (MX) has a \( S^2 \) value of 2.60]. For Chichibabin analogue, we freeze the core electrons.

The Cartesian geometries of all systems are given in the supplementary material. For benzenes, we used the SF-CCSD/aug-cc-pVTZ optimized geometry of the ground state \( (1\text{A}1 \text{in o-/m-benzyne and 1A}_g \text{in p-benzyne}) \) from Ref. 39. For MX and its analogues as well as for PQM and Chichibabin analogue, we used the CCSD/6-31G(d) optimized geometry of the triplet reference state. We note that Q-Chem does not follow the standard Mulliken convention\(^{87,88}\) for molecular orientation, consequently, some symmetry labels differ from the standard notations. Systems with the \( C_{2v} \) point group (o-/m-benzenes, MX and its analogues) are oriented in the \( xz \)-plane with the \( C_{2z} \)-axis along the \( z \)-axis. \( \rho \)-Benzyne (\( D_{2h} \) point group) is in the \( xy \)-plane, with the \( y \)-axis passing through the diradical centers. PQM and the Chichibabin analogue (both \( D_{2h} \) point group) are oriented in the \( xy \)-plane, with the \( x \)-axis passing through the diradical centers.

We computed static polarizabilities of the lowest closed-shell and open-shell singlet states and compared them with those of the high-spin triplet reference and low-spin triplet states. We also calculated 2PA cross sections between the two lowest closed-shell singlet states and between the lowest closed-shell singlet and open-shell singlet states.

To rationalize the trends in the computed response properties, we construct few-states models by evaluating individual terms in the sum-over-states expressions. For this semi-quantitative analysis, we calculated unrelaxed transition dipole moments (without orbital relaxation and amplitude response) at the same level of theory and basis set. We also calculated the Head-Gordon indices using the wave-function-analysis tools available in Q-Chem.\(^{89,90}\)

IV. RESULTS AND DISCUSSION

A. Benzenes

The calculated energies and static polarizabilities for the lowest electronic states of benzyne diradicals are given in Table I. The \( S^2 \) values of these states are given in the supplementary material. We note that although \( S^2 \) for the SF states from the primary diradical manifold (and the UHF reference) show small deviations in the 0.00 to 0.21 range, other SF states, unsurprisingly, show larger deviations and the impact of their spin contamination on the response properties is unclear.
In each of the benzyne diradicals, the static polarizability of the closed-shell singlet ground state (X\(^1\)\(\text{A}_g\) in \(p\)-benzyne, \(X\(^1\)\(\text{A}_1\) in \(o\)-benzyne/m-benzyne) is similar to that of the high-spin reference and lowest low-spin triplet states. However, for the lowest open-shell singlet state (\(1\)\(\text{B}_2\) in \(p\)-benzyne, \(1\)\(\text{B}_1\) in \(o\)-benzyne/m-benzyne), \(\alpha_{xy}\) for \(p\)-benzyne and \(\alpha_{xx}\) for \(o\)-benzyne and \(m\)-benzyne are significantly larger than the corresponding values in the ground state and the two triplet states. This is expected, as the ground state is dipole-coupled to the lowest \(1\)\(\text{B}_2\) (or \(1\)\(\text{B}_1\)) state, while the lowest \(1\)\(\text{B}_2\) (or \(1\)\(\text{B}_1\)) state is also dipole-coupled to the higher \(\text{A}_g\) (or \(\text{A}_1\)) state. This result can be rationalized with few-states models involving the lowest dipole-coupled states for each system as shown in Fig. 2.

For systems with \(C_{2v}\) point group (\(o\)-benzyne and \(m\)-benzyne), \(\text{A}_1\) and \(\text{B}_1\) states are dipole-coupled via the \(x\)-component of the dipole moment operator. The sum-over-states expression for the \(xx\)-component of the static polarizability [Eq. (10)] for an \(\text{A}_1\) state only involves the sum over all \(\text{B}_1\) states and vice versa, as the \(x\)-components of the transition moments involving states of other symmetry representations are zero by symmetry. Similarly, by symmetry, the sum-over-states expressions for \(\alpha_{yy}\) of \(\text{A}_g\) and \(\text{B}_{2u}\) states in \(p\)-benzyne (\(D_{2h}\) point group) involve only the sums over \(\text{B}_{2u}\) and \(\text{A}_g\) states, respectively. In the few-states models, we exploit these symmetry restrictions and include only the lowest few \(\text{A}_1\) and \(\text{B}_1\) states for \(o\)-benzyne and \(m\)-benzyne and lowest few \(\text{A}_g\) and \(\text{B}_{2u}\) states for \(p\)-benzyne. Figure 2 also gives the contribution of each term in the sum-over-states expression to the polarizability.

For \(o\)-benzyne, the few-states model shows that the large increase in \(\alpha_{xx}\) of the lowest \(1\)\(\text{B}_1\) state arises mainly due to its large transition dipole and a small energy gap with the \(1\)\(\text{A}_1\) state with an excited energy of 6.19 eV [the second closed-shell singlet (CSS2) state based on the \(S^2\) values given in the supplementary material], providing a significant contribution to the sum-over-states. In contrast, the contribution arising from the ground state (\(X\(^1\)\(\text{A}_1\)) is relatively small and negative (the same contribution with an opposite sign is present in the sum-over-states expression of the ground state).

For \(m\)-benzyne, the few-states analysis reveals that the sum-over-states expression for \(\alpha_{xy}\) of the lowest \(1\)\(\text{B}_1\) state has two significant contributions arising due to two \(\text{A}_1\) states with excitation energies of 5.85 eV and 6.92 eV, which results in a large increase of this component relative to the ground state. (We note that the four excited \(\text{A}_1\) states computed here show significant spin contamination: \(S^2\) are 1.12, 1.46, 1.55, and 0.64.)

\(p\)-Benzyne is similar to \(o\)-benzyne; larger \(\alpha_{yy}\) for the lowest \(1\)\(\text{B}_{2u}\) state is a consequence of a stronger dipole coupling and a smaller energy gap with the second closed-shell singlet state (\(1\)\(\text{A}_g\) with an excitation energy of 4.90 eV), relative to the ground state.

The changes from the ground state to the open-shell singlet in the above components of the static polarizability are largest for \(p\)-benzyne (\(\alpha_{yy}\) changes from 78.4 a.u. to 1920.6 a.u.) and smallest for \(o\)-benzyne (\(\alpha_{xx}\) changes from 83.3 a.u. to 137.2 a.u.). The few-states models (Fig. 2) show that the primary reason for this trend is the increasing transition dipole moment and decreasing energy difference between the open-shell singlet and the second closed-shell singlet states as the distance between the radical centers increases from \(o\)-benzyne to \(p\)-benzyne. This increase in the transition dipole moment with the distance between the radical centers can be rationalized by analyzing the expressions for the transition moments between the open-shell singlet and the closed-shell singlets [Eqs. (15) and (19)] using the two-electrons-in-two-molecular-orbitals picture described in Sec. II D. The two MOs that host the unpaired electrons are of \(\sigma\) and \(\sigma^*\) character (shown in Fig. 3), deriving from the \(sp^2\)-orbitals, \(\chi_1\) and \(\chi_2\), localized on the radical centers as per Eqs. (16) and (17). Thus, Eqs. (18) and (20) explain why the transition dipole moments between the open-shell singlet states and the second closed-shell singlet increase as the distance between the radical centers increases from \(o\)-benzyne to \(p\)-benzyne.

Table II presents the 2PA cross sections and transition moments with degenerate photons for transitions from the closed-shell singlet (CSS1) ground states to the second closed-shell singlet (CSS2) states or the open-shell singlet (OSS) states in benzyynes. The large spin contamination in the higher SF states in \(m\)-benzyne makes the identification of the second closed-shell diradical singlet state difficult. We do not include the 2PA analysis for the transition between the ground state and second closed-shell singlet state for \(m\)-benzyne here. The

### Table I: Excitation energies (in eV) and static polarizabilities (in a.u.) of the high-spin (\(M_s = 1\)) triplet reference, \(M_s = 0\) triplet state, open-shell singlet state, and lowest closed-shell singlet states of \(o\)-benzyne, \(m\)-benzyne, and \(p\)-benzyne calculated with EOM-SF-CCSD/aug-cc-pVDZ.

<table>
<thead>
<tr>
<th></th>
<th>(M_s = 1)</th>
<th>(M_s = 0)</th>
<th>OSS</th>
<th>CSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{ex})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{xx})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{yy})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{zz})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{is})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{ps})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>(M_s = 1)</th>
<th>(M_s = 0)</th>
<th>OSS</th>
<th>CSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{ex})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{xx})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{yy})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{zz})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{is})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{ps})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>(M_s = 1)</th>
<th>(M_s = 0)</th>
<th>OSS</th>
<th>CSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{ex})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{xx})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{yy})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{zz})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{is})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha_{ps})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIG. 2. Few-states models for static polarizabilities of benzyne diradicals. Energy levels are relative to the energy of the ground state (\(X^1A_1\) or \(X^1A_g\)). Terms in the sum-over-states expression of \(\alpha_{xx}\) for the lowest closed-shell singlet (\(X^1A_1\)) and open-shell singlet (lowest \(1B_1\)) states in \(o\)-benzyne and \(m\)-benzyne and \(\alpha_{yy}\) for the same (\(X^1A_g\) and lowest \(1B_2\)) states in \(p\)-benzyne are shown. Numbers in black denote contributions to \(\alpha_{xx}\) of the \(X^1A_1\) state or \(\alpha_{yy}\) of the \(X^1A_g\) state. Numbers in magenta denote contributions to \(\alpha_{xx}\) of the lowest \(1B_1\) state or \(\alpha_{yy}\) of the lowest \(1B_2\) state.

fully symmetric transitions in \(o\)-benzyne and \(p\)-benzyne show larger cross sections (\(\sigma^{2PA}\) in a.u.) than the non-fully symmetric transitions, as can be rationalized by the symmetry analysis.\(^{27}\) Note that, despite the increased 2PA transition moments, the macroscopic 2PA cross sections (\(\sigma^{2PA}\) in GM) for all these transitions are small because of the low transition energies. The fully symmetric transitions feature larger individual components in the 2PA transition dipole moment matrix, \(M_{aa}\) in \(o\)-benzyne and \(M_{yy}\) in \(p\)-benzyne. The few-states models for these two 2PA transition moments shown in Fig. 4 indicate that these are dominated by the contribution of the sum-over-states term involving the lowest \(1B_1\) and \(1B_{2u}\) states, respectively. This is a consequence of larger dipole couplings of the initial (CSS1) and final (CSS2) states with the lowest \(1B_1\) or \(1B_{2u}\) states (OSS) present in the numerator of these sum-over-states terms. For degenerate 2PA in benzenes, the differences between the photon energy and the energy gaps of the lowest \(1B_1\) or \(1B_{2u}\) state relative to the ground state are significant (~1-2 eV); hence the 2PA cross sections are smaller due to the lack of near-resonance enhancement.

Since the sum-over-states for the CSS1 \(\rightarrow\) CSS2 transitions in \(o\)-benzyne and \(p\)-benzyne is dominated by the term involving the OSS state, the corresponding 2PA transition moments can be approximated as follows:

\[
M_{\text{CSS2\rightarrow CSS1}}^{\text{CSS2\rightarrow CSS1}}(n = \text{OSS}) \approx -2 \frac{(\text{CSS2}|\mu_a|\text{OSS})(\text{OSS}|\mu_a|\text{CSS1})}{E_{\text{OSS}} - E_{\text{CSS1}} - \omega},
\]

(26)

where \(a\) denotes a Cartesian component. From Eqs. (18) and (20), we obtain

\[
M_{\text{CSS2\rightarrow CSS1}}^{\text{CSS2\rightarrow CSS1}}(n = \text{OSS}) \approx - \frac{1 - \lambda^2}{8 (1 + \lambda^2)} \frac{R_{12}^2}{E_{\text{OSS}} - E_{\text{CSS1}} - \omega}.
\]

(27)

Equation (27) suggests that the 2PA transition moments increase with decreasing values of \(\lambda\) and increasing distance...
between the radical centers. While the distance between the radical centers increases from \( o \)-benzene to \( p \)-benzene, the corresponding increase in the 2PA transition moment is partially negated by the increase in the diradical character from \( o \)-benzene to \( p \)-benzene. Nevertheless, we see that \( M_{yy} \) in \( p \)-benzene is larger than \( M_{xx} \) in \( o \)-benzene.

### B. Meta-xylylene and its analogues

The \( m \)-xylylene (MX) diradical and several of its analogues are shown in Fig. 5. The character of the lowest singlet and triplet electronic states and their ordering in these systems have been studied before.\(^{45}\) The MOs hosting the unpaired electrons are shown in Fig. 6. In all MX analogues studied here, the frontier MOs are similar in character. As discussed in Ref. 45, due to different nodal structures of these MOs at the ortho position relative to the CH2 groups, different substituents at this position will affect the electronic structure and properties of these systems. For example, it was noted in Ref. 45 that stabilizing the \( b_2 \) orbital (note that we follow different symmetry convention in this study compared to Ref. 45 such that \( b_1 \) orbital in Ref. 45 shows up as \( b_2 \) orbital here) would decrease the diradical character, increase the singlet-triplet gap, and result in a singlet ground state. MX, MX2, and MX3 show a triplet ground state consistent with Hund’s rule, which predicts high-spin coupling in the ground state for diradicals in which the nearly degenerate MOs that host the unpaired electrons overlap in space. In violation of Hund’s rule, MX4 and MX5 with charged substituents have a singlet ground state. In Ref. 45, this preferential stabilization of the singlet state in MX4 and MX5 due to different substituents was explained by the resonance stabilization due to additional closed-shell configurations. However, it was noted that resonance theory fails to explain why the open-shell singlet was the lowest singlet state in MX3.

Here, we investigate the effects of substituents on the response properties of the electronic states in these systems. As done for benzenes, we explain the trends in the calculated polarizabilities by constructing few-states models based on the sum-over-states expressions. In the Hückel model for MX, the \( b_2 \) and \( a_2 \) MOs can be expressed in term of the AOs (\( p \)-orbitals on the carbons forming \( \pi \)-conjugation) as follows:

\[
b_2 = \frac{1}{\sqrt{3}} (p_1 + p_5 - p_3), \quad \quad (28)
\]

\[
a_2 = \frac{1}{2} (p_1 - p_5 + p_6 - p_8). \quad \quad (29)
\]

Substituting Eqs. (28) and (29) in Eq. (15), we obtain the transition dipole moment between the open-shell singlet and lowest closed-shell singlet states as follows:

\[
\langle \Psi_{\text{OSS}} | \mu | \Psi_{\text{CSS1}} \rangle = \frac{1}{2 \sqrt{1 + \lambda^2}} (1 - \lambda) \left( b_2 | \mu | a_2 \right)
\]

\[
= \frac{1}{2 \sqrt{1 + \lambda^2}} (1 - \lambda) \left( \frac{1}{\sqrt{3}} (p_1 + p_5 - p_3) \right)
\]

\[
\times |\mu| (p_1 - p_5 + p_6 - p_8)
\]

\[
\approx \frac{1}{4 \sqrt{3} + 3 \lambda^2} (1 - \lambda) \left( (p_1 | \mu | p_1) - (p_5 | \mu | p_5) \right),
\]

(30)

---

**TABLE II. 2PA cross sections (\( \delta^{2PA} \)) and transition moments (\( M_{ij} \)) for the CSS1 \( \rightarrow \) CSS2 and CSS1 \( \rightarrow \) OSS transitions in benzyne diradicals.** Frequencies of degenerate photons (\( \omega = \frac{E_i + E_f}{2} \)) are given in electron-volts. \( \sigma^{2PA} \) are given in GM. All other values are in a.u.

<table>
<thead>
<tr>
<th></th>
<th>CSS1 ( \rightarrow ) CSS2</th>
<th></th>
<th>CSS1 ( \rightarrow ) OSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega )</td>
<td>( \delta^{2PA} )</td>
<td>( \sigma^{2PA} )</td>
<td>( M_{xx}^{\text{e-i}} )</td>
</tr>
<tr>
<td>----------------</td>
<td>-------------------------------</td>
<td>-----------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>( o )-benzene</td>
<td>3.10</td>
<td>182</td>
<td>3</td>
</tr>
<tr>
<td>( m )-benzene</td>
<td>2.45</td>
<td>764</td>
<td>7</td>
</tr>
</tbody>
</table>

---

**FIG. 4.** Few-states models for 2PA transition moments for the CSS1 \( \rightarrow \) CSS2 transition in \( o \)-benzene and \( p \)-benzene diradicals. The 2PA transition moments for the corresponding CSS1 \( \leftarrow \) CSS2 transitions give the same qualitative picture and are not shown. Terms in the sum-over-states expression of \( M_{xx} \) in \( o \)-benzene and \( M_{yy} \) in \( p \)-benzene are shown in black. All numbers are in a.u. The dominant contribution to each of these 2PA transition moments arises from the sum-over-states term involving the OSS (lowest \( ^1B_1 \) or \( ^1B_{2u} \)) state.
which is similar to Eq. (18) (note that the $p$-orbitals in the above equation are localized on the carbons and have negligible overlap thereby giving negligible contribution to the transition dipole moment). This transition dipole moment increases with decreasing diradical character (or $\lambda$) for a constant distance between the radical centers. Similarly, from Eqs. (28), (29), and (19), the transition dipole moment between the open-shell singlet and second closed-shell singlet states is given as follows:

$$\langle \Psi_{OSS} | \mu | \Psi_{CSS2} \rangle \approx \frac{1}{4\sqrt{3} + 3\lambda^2} (1 + \lambda)(\langle p_1 | \mu | p_1 \rangle - \langle p_5 | \mu | p_5 \rangle),$$

(31)

which is similar to Eq. (20). This transition dipole moment decreases with decreasing diradical character (or $\lambda$) for a constant distance between the radical centers. In the structures of MX and its analogues studied here, the distance between the radical centers is similar (4.70–4.94 Å). Thus, the transition dipole moments in these systems change primarily due to changes in the diradical character $\lambda$. Since these transition dipoles affect the polarizabilities (in the sum-over-states expressions), we expect the polarizabilities to be affected by the change in $\lambda$ in this set of diradicals. Note that the lone pair on oxygen participates in the $\pi$-conjugation in MX5, however, we neglect the small changes in the normalization coefficients in Eqs. (28) and (29) when analyzing qualitative trends in the transition dipole moments.

The energies and static polarizabilities of the electronic states of MX and its analogues are collected in Table III. The few-states models are shown in Fig. 7. We also report $S^2$ for all the states used in the few-states model in the supplementary material and note that some of these SF states show large spin contamination. We give the approximate values of $\lambda$ for each system in Table IV. These $\lambda$s were computed by taking the ratios of the EOM amplitudes $\phi_1 \rightarrow \phi_2$ and $\phi_2 \rightarrow \phi_1$ for the corresponding lowest closed-shell singlet states. We also provide the $n_{u,nl}$ values for the lowest closed-shell singlet states. The computed $n_{u,nl}$ values compare well with the values calculated using Eq. (25) for larger values of $\lambda$s but not for smaller $\lambda$s. As pointed out above, Head-Gordon’s index provides a more robust measure of the diradical character than the wave-function amplitudes.

The lowest singlet state in MX is the closed-shell singlet state ($^1A_1$) with static polarizability similar to that of the triplet ground state. The next lowest singlet state is the open-shell

<table>
<thead>
<tr>
<th>MX</th>
<th>$M_f = 1$</th>
<th>$M_f = 0$</th>
<th>OSS</th>
<th>CSS1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle \Psi_{OSS}</td>
<td>\mu</td>
<td>\Psi_{CSS2} \rangle$</td>
<td>$\langle \Psi_{OSS}</td>
<td>\mu</td>
</tr>
<tr>
<td>3B_1</td>
<td>3B_1</td>
<td>1B_1</td>
<td>1B_1</td>
<td></td>
</tr>
<tr>
<td>$E_{ex}$</td>
<td>0.00</td>
<td>0.00</td>
<td>1.69</td>
<td>0.57</td>
</tr>
<tr>
<td>$\alpha_{xx}$</td>
<td>140.8</td>
<td>140.7</td>
<td>329.3</td>
<td>142.2</td>
</tr>
<tr>
<td>$\alpha_{yy}$</td>
<td>60.0</td>
<td>60.0</td>
<td>63.3</td>
<td>60.9</td>
</tr>
<tr>
<td>$\alpha_{zz}$</td>
<td>104.3</td>
<td>104.2</td>
<td>105.5</td>
<td>126.3</td>
</tr>
<tr>
<td>$\alpha_{iso}$</td>
<td>101.7</td>
<td>101.7</td>
<td>166.0</td>
<td>109.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MX2</th>
<th>$M_f = 1$</th>
<th>$M_f = 0$</th>
<th>OSS</th>
<th>CSS1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle \Psi_{OSS}</td>
<td>\mu</td>
<td>\Psi_{CSS2} \rangle$</td>
<td>$\langle \Psi_{OSS}</td>
<td>\mu</td>
</tr>
<tr>
<td>$E_{ex}$</td>
<td>0.00</td>
<td>0.00</td>
<td>1.83</td>
<td>0.46</td>
</tr>
<tr>
<td>$\alpha_{xx}$</td>
<td>133.2</td>
<td>133.1</td>
<td>296.7</td>
<td>143.6</td>
</tr>
<tr>
<td>$\alpha_{yy}$</td>
<td>56.9</td>
<td>56.9</td>
<td>59.9</td>
<td>57.7</td>
</tr>
<tr>
<td>$\alpha_{zz}$</td>
<td>100.8</td>
<td>100.8</td>
<td>102.3</td>
<td>118.5</td>
</tr>
<tr>
<td>$\alpha_{iso}$</td>
<td>96.9</td>
<td>96.9</td>
<td>153.0</td>
<td>106.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MX3</th>
<th>$M_f = 1$</th>
<th>$M_f = 0$</th>
<th>OSS</th>
<th>CSS1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle \Psi_{OSS}</td>
<td>\mu</td>
<td>\Psi_{CSS2} \rangle$</td>
<td>$\langle \Psi_{OSS}</td>
<td>\mu</td>
</tr>
<tr>
<td>$E_{ex}$</td>
<td>0.00</td>
<td>0.00</td>
<td>0.57</td>
<td>1.21</td>
</tr>
<tr>
<td>$\alpha_{xx}$</td>
<td>140.3</td>
<td>140.3</td>
<td>196.5</td>
<td>141.6</td>
</tr>
<tr>
<td>$\alpha_{yy}$</td>
<td>59.0</td>
<td>59.0</td>
<td>60.6</td>
<td>60.6</td>
</tr>
<tr>
<td>$\alpha_{zz}$</td>
<td>112.7</td>
<td>112.7</td>
<td>111.7</td>
<td>184.8</td>
</tr>
<tr>
<td>$\alpha_{iso}$</td>
<td>104.0</td>
<td>104.0</td>
<td>122.9</td>
<td>129.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MX4</th>
<th>$M_f = 1$</th>
<th>$M_f = 0$</th>
<th>OSS</th>
<th>CSS1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle \Psi_{OSS}</td>
<td>\mu</td>
<td>\Psi_{CSS2} \rangle$</td>
<td>$\langle \Psi_{OSS}</td>
<td>\mu</td>
</tr>
<tr>
<td>$E_{ex}$</td>
<td>0.00</td>
<td>0.00</td>
<td>1.94</td>
<td>0.06</td>
</tr>
<tr>
<td>$\alpha_{xx}$</td>
<td>129.1</td>
<td>129.1</td>
<td>260.8</td>
<td>159.0</td>
</tr>
<tr>
<td>$\alpha_{yy}$</td>
<td>49.1</td>
<td>49.1</td>
<td>50.6</td>
<td>49.5</td>
</tr>
<tr>
<td>$\alpha_{zz}$</td>
<td>96.6</td>
<td>96.6</td>
<td>95.3</td>
<td>102.8</td>
</tr>
<tr>
<td>$\alpha_{iso}$</td>
<td>91.6</td>
<td>91.6</td>
<td>135.6</td>
<td>103.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MX5</th>
<th>$M_f = 1$</th>
<th>$M_f = 0$</th>
<th>OSS</th>
<th>CSS1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle \Psi_{OSS}</td>
<td>\mu</td>
<td>\Psi_{CSS2} \rangle$</td>
<td>$\langle \Psi_{OSS}</td>
<td>\mu</td>
</tr>
<tr>
<td>$E_{ex}$</td>
<td>0.00</td>
<td>0.00</td>
<td>1.27</td>
<td>0.14</td>
</tr>
<tr>
<td>$\alpha_{xx}$</td>
<td>196.6</td>
<td>196.5</td>
<td>290.7</td>
<td>243.8</td>
</tr>
<tr>
<td>$\alpha_{yy}$</td>
<td>86.3</td>
<td>86.3</td>
<td>167.4</td>
<td>81.1</td>
</tr>
<tr>
<td>$\alpha_{zz}$</td>
<td>142.5</td>
<td>142.5</td>
<td>140.5</td>
<td>148.8</td>
</tr>
<tr>
<td>$\alpha_{iso}$</td>
<td>141.8</td>
<td>141.8</td>
<td>199.5</td>
<td>157.9</td>
</tr>
</tbody>
</table>

FIG. 5. Meta-xylene diradical and its analogues.

FIG. 6. Frontier MOs of the m-xylene diradical.
singlet state ($^1B_1$) with a significantly different $\alpha_{xx}$ compared to those of the triplet and lowest $^1A_1$ states. The few-states model for MX suggests that the sum-over-states term involving the second closed-shell singlet (CSS2) state ($^1A_1$ state with an excitation energy of 3.06 eV) has the dominating contribution to $\alpha_{xx}$ of the OSS state, while the contribution from the lowest $^1A_1$ (CSS1) state is small. This is because of the large transition dipole moment and small energy difference between the OSS and CSS2 states. This is also consistent with the fact that $\lambda$ for MX is almost 1 ($n_{u,nl}$ is almost 2), which means that the coupling of the open-shell singlet state with the lowest closed-shell state does not significantly affect the static polarizabilities of either state.

The ground state in MX2 is, again, triplet and the lowest singlet state is the closed-shell state ($^1A_1$). For MX2, $\lambda$ decreases to about 0.8 ($n_{u,nl}$ drops to 1.8), which causes an increase in the transition dipole moment between the open-shell singlet state ($^1B_1$) and the lowest closed-shell singlet state consistent with Eq. (30). $\alpha_{xx}$ for the lowest closed-shell singlet state is slightly different from the triplet state, however, due to the smaller $\lambda$, the difference in $\alpha_{xx}$ between the CSS1 and OSS states is smaller than in MX. This is because larger coupling in MX2 relative to MX between the OSS and CSS1 states contributes a larger positive term to $\alpha_{xx}$ of the CSS1 state and an equally negative term (the CSS1 state is lower in energy than the OSS state in MX2) to $\alpha_{xx}$ of the OSS state. In addition, the transition dipole between the OSS state and CSS2 state ($^1A_1$ with an excitation energy of 2.98 eV) decreases according to Eq. (31) and this coupling has a smaller effect on the polarizability of the OSS state compared to that in MX.

The ground state in MX3 is triplet, but the lowest singlet is open-shell ($^1B_1$ state with an excitation energy of 0.57 eV). For MX3, $\lambda$ is almost equal to 1, which, again, indicates smaller dipole coupling of this OSS state with the lowest closed-shell singlet state ($^1A_1$ state with an excitation energy of 1.21 eV) and a larger dipole coupling with the second closed-shell singlet state ($^1A_1$ state with an excitation energy of 2.78 eV) according to Eqs. (30) and (31). However, the dipole coupling between the OSS and CSS2 states is slightly smaller than that of MX2. Nevertheless, the contribution from the coupling with the CSS2 state dominates the sum-over-states expression for $\alpha_{xx}$ of the OSS state, although a relatively larger energy difference in the denominator restricts the difference between the $\alpha_{xx}$ values of the OSS and CSS1 states to a value smaller than those of MX and MX2. We also note here that significantly different $\alpha_{xx}$ for CSS1 is because of its stronger coupling and smaller energy difference with the CSS2 state.

MX4 and MX5 have closed-shell singlet ground states ($^1A_1$ states with energies 0.06 eV and 0.14 eV below the triplet states, respectively), consistent with smaller values of $\lambda$ and
\[
M_{xx}^{\text{CSS2} \rightarrow \text{CSS1}} (n = \text{OSS}) \approx -\frac{1}{24 (1 + \lambda^2) (1 - \lambda^2)} \times \frac{(\langle p_5 | X | p_5 \rangle - \langle p_1 | X | p_1 \rangle)^2}{E_{\text{OSS}} - E_{\text{CSS1}} - \omega}. \tag{32}
\]

Equation (32) suggests that the numerators of these 2PA transition moments increase with decreasing values of \(\lambda\) for a constant distance between the radical centers. This trend is indeed observed in the few-states models. While the numerator increases when we go from MX3 to MX to MX2 to MX4 to MX5 as the \(\lambda\) decreases, the denominator (difference between the photon energy and \(E_{\text{OSS}} - E_{\text{CSS1}}\)) is the smallest for MX2 as the OSS state lies almost midway between the two \(1^1A_1\) states. Therefore, MX2 shows the largest \(M_{xx}\) and \(\sigma_{2PA}\) for the CSS1 \(\rightarrow\) CSS2 transition due to near-resonance enhancement. \(M_{xx}\) for the CSS1 \(\rightarrow\) CSS2 transition in MX5 shows a larger numerator (consistent with a smaller \(\lambda\)) and a smaller denominator than these values in MX4. As a result, MX5 shows larger \(M_{xx}\) and \(\sigma_{2PA}\) for this transition. While the denominator in the case of MX is smaller compared to MX4 and MX5, the smaller coupling strength of the OSS state with the CSS1 state due to a higher \(\lambda\) restricts its \(M_{xx}\) and \(\sigma_{2PA}\) to a smaller value compared to MX4 and MX5. In MX3, the OSS state is lower than the two \(1^1A_1\) states and, hence, the energy of this state is negative relative to the CSS1 state, giving a large negative denominator in Eq. (32). In addition, MX3 has \(\lambda\) almost equal to 1, thereby, the dipole couplings of the OSS state with \(n_{nl}\) relative to other systems. Consequently, in these systems, the dipole couplings of the OSS states (\(1^1B_1\) states with excitation energies of 1.94 eV and 1.27 eV relative to the triplet states) with the ground states is large, which makes a large positive contribution to \(\alpha_{xx}\) of the ground states and a large negative contribution to \(\alpha_{xx}\) of the OSS states in these systems. In addition, according to Eq. (31), the contribution to \(\alpha_{xx}\) of OSS states from the couplings with the CSS2 states (\(1^1A_1\) states with excitation energies of 2.58 eV and 1.94 eV) decreases with decreasing \(\lambda\). The larger the values of \(\alpha_{xx}\) between the CSS1 and OSS states shrinks (smallest for MX5 with smallest \(\lambda\)), compared to these differences in MX and MX2.

The 2PA cross sections \((\sigma_{2PA})\) with degenerate photons for the CSS1 \(\rightarrow\) CSS2 and CSS1 \(\rightarrow\) OSS transitions in these systems are given in Table V. Except for MX3, \(\sigma_{2PA}\) for the fully symmetric CSS1 \(\rightarrow\) CSS2 transitions are significantly larger. These transitions feature large 2PA transition moments \(M_{xx}\), which is a consequence of either the strong coupling of one or both of these states with the OSS states and/or small differences in energies of the photons and the relative energies of these states with the OSS states based on the few-states models shown in Fig. 8. In fact, in each of MX, MX2, MX4, and MX5, the contribution to the sum-over-states for the 2PA transition moment \(M_{xx}\) for the CSS1 \(\rightarrow\) CSS2 transition from the term involving the OSS state dominates. As a result, these \(M_{xx}\) can be approximated using Eq. (26). From Eqs. (26), (30), and (31), we obtain

\[
M_{xx}^{\text{CSS2} \rightarrow \text{CSS1}} = -98.4 \quad M_{xx}^{\text{CSS2} \rightarrow \text{CSS1}} = -484.5 \quad M_{xx}^{\text{CSS2} \rightarrow \text{CSS1}} = -16.2 \quad M_{xx}^{\text{CSS2} \rightarrow \text{CSS1}} = -142.8 \quad M_{xx}^{\text{CSS2} \rightarrow \text{CSS1}} = 263.0
\]
TABLE VI. Head-Gordon’s indices and approximate values of $\alpha_u$ for the lowest singlet states of PQM and CCB1. Here, $\lambda = R_{\phi_1 \rightarrow \phi_2} R_{\phi_2 \rightarrow \phi_1}^{-1}$. $\alpha_u$ values are given in the supplementary material.

<table>
<thead>
<tr>
<th>Radical</th>
<th>$\phi_1$</th>
<th>$\phi_2$</th>
<th>$R_{\phi_2 \rightarrow \phi_1}$</th>
<th>$R_{\phi_1 \rightarrow \phi_2}$</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PQM</td>
<td>$2b_{1u}$</td>
<td>$2b_{2g}$</td>
<td>0.83</td>
<td>0.19</td>
<td>0.23</td>
</tr>
<tr>
<td>CCB1</td>
<td>$3b_{1u}$</td>
<td>$3b_{2g}$</td>
<td>0.72</td>
<td>0.38</td>
<td>0.53</td>
</tr>
</tbody>
</table>

C. Para-quinodimethane and Chichibabin analogue

To further investigate the correlation between the diradical character and the response properties, we calculated the static polarizabilities and 2PA cross sections of para-quinodimethane (PQM) and extended PQM (Chichibabin’s hydrocarbon without the phenyls, denoted CCB1). The closed-shell quinoid and open-shell nonquinoidal resonance structures of these systems are shown in Fig. 9. Table VI lists relevant wave function parameters and Head-Gordon’s index for the lowest singlet states. The diradical character in both species is considerably reduced relative to MX; in the latter, the number of unpaired electrons is ~2, whereas PQM and CCB1 have 0.6 and 1.4 unpaired electrons, respectively. The reduced diradical character can be explained by the resonance stabilization of the closed-shell configuration due to the quinoid form (Fig. 9). The diradical character (as quantified by the $\lambda$ and $\alpha_u$ values) in CCB1 is greater than in PQM because of the quinoid form's competition with two aromatic rings rather than one.

Excitation energies and static polarizabilities for the electronic states of PQM and CCB1 are given in Table VII. $S^2$ values are given in the supplementary material. For PQM, the closed-shell ground state ($X^1A_g$) or CSS1 shows different $\alpha_u$ than the triplet states. The open-shell singlet excited state ($^1B_{3u}$ state with an excitation energy of 4.84 eV) shows significantly larger $\alpha_u$. The difference in $\alpha_u$ between the OSS and CSS1 states is significantly larger than the difference in $\alpha_u$ between the OSS and CSS1 states of MX. The few-states model for PQM shown in Fig. 10 suggests that the dominant contribution to the sum-over-states expression for $\alpha_u$ of the OSS state arises due to its dipole coupling with the $A_g$ state with an excitation energy of 5.64 eV, although contributions due to the coupling with other $A_g$ states are also non-negligible. Because of the reduced diradical character, neither PQM nor CCB1 have low-lying states that can be described as CSS2. Rather, the doubly excited configurations appear to be contributing to multiple $A_g$ states. Thus, we analyze the transition dipole moments between the OSS state and the lowest $A_g$ states. Based on the analysis in Sec. IID of the effect of the diradical character on transition dipole moments between the CSS1 state and the OSS state, we expect larger values for these transition moments. While decreasing the diradical character would decrease the transition dipole moments between the OSS state and second closed-shell singlet state, the increased distance between the carbons hosting the unpaired electrons would have the opposite effect (relative to MX, these transition moments are larger in PQM). The largest contribution to the OSS polarizability from the closest $A_g$ state (located at 4.54 eV in Fig. 10) is from an excitation of 5.64 eV, which can be rationalized by large dipole coupling and small energy denominator. Note, however, that the next $A_g$ state, located only 0.16 eV above, contributes much less.

TABLE VII. Excitation energies (in eV) and static polarizabilities (in a.u.) of the high-spin ($M_s = 1$) triplet reference, $M_s = 0$ triplet state, open-shell singlet state, and lowest closed-shell singlet states of PQM and CCB1 calculated with EOM-SF-CCSD/aug-cc-pVDZ.

<table>
<thead>
<tr>
<th></th>
<th>PQM</th>
<th>CCB1</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSS</td>
<td>$^1A_g$</td>
<td>CSS</td>
</tr>
<tr>
<td>$E_g$</td>
<td>1.10</td>
<td>1.10</td>
</tr>
<tr>
<td>$\alpha_u$</td>
<td>151.1</td>
<td>151.1</td>
</tr>
<tr>
<td>$\alpha_u$</td>
<td>98.5</td>
<td>98.5</td>
</tr>
<tr>
<td>$\alpha_u$</td>
<td>60.7</td>
<td>60.7</td>
</tr>
<tr>
<td>$\alpha_u$</td>
<td>103.5</td>
<td>103.5</td>
</tr>
</tbody>
</table>
FIG. 10. Few-states model for static polarizabilities of \( p \)-quinodimethane. Energy levels are relative to the energy of the lowest \( ^3B_{3u} \) state. Terms in the sum-over-states expression of \( \alpha_{xx} \) are shown. Numbers in black denote contributions to \( \alpha_{xx} \) of \( ^1A_g \) state. Numbers in magenta denote contributions to \( \alpha_{xx} \) of \( ^1B_{3u} \) state. All numbers are in a.u. (Absolute values of the transition moments in the sum-over-states terms are reported.)

This analysis emphasizes the need for computing the actual polarizabilities rather than guessing the trends from few-states models.

For CCB1, static polarizabilities for the closed-shell singlet ground \( ^1A_g \) state or CSS1 and triplet states are presented (we do not report the polarizability of the open-shell singlet state due to problems with convergence of the response equations). The difference in the \( \alpha_{xx} \) value for the ground state and the triplet states is larger for CCB1 than that in PQM. The \( \alpha_{xx} \) values for all these electronic states in CCB1 are larger than that of the corresponding states in PQM. This is because of the larger distance between the carbon centers hosting the unpaired electrons in CCB1.

2PA transitions between gerade and ungerade states are forbidden. For PQM (\( D_{2h} \) symmetry), the 2PA cross section with degenerate photons for the CSS1 \( \rightarrow A_g (5.64 \text{ eV}) \) transition is given in Table VIII. This cross section is larger than the cross section for the transition between the two lowest closed-shell singlet states in MX. Similar to MX, this transition features large 2PA transition moments, \( M_{xx} \), which are dominated by a single term involving the OSS state in the few-states model shown in Fig. 11. However, unlike the case of MX, a large \( M_{xx} \) value is a consequence of larger transition dipole moments (due to the longer distance between the radical centers and smaller \( \lambda \)) of both the initial and final states with the OSS state, even though the difference in the photon energy and the energy gap between the CSS1 and OSS states is relatively large.

FIG. 11. Few-states models for 2PA transition moments for the CSS1 \( \rightarrow A_g (5.64 \text{ eV}) \) transition in \( p \)-quinodimethane. The 2PA transition moments for the CSS1 \( \rightarrow A_g (5.64 \text{ eV}) \) transitions give the same qualitative picture and are not shown. Energy levels are relative to the energy of the lowest \( ^1B_{3u} \) state. Numbers in black denote contributions to \( M_{xx} \) of OSS \( ^1B_{3u} \) state.

**TABLE VIII.** 2PA cross sections (\( \sigma^{2PA} \)) and transition moments (\( M_{xx}^{(i,j)} \)) for the CSS1 \( \rightarrow A_g (5.64 \text{ eV}) \) transition in PQM and CSS1 \( \rightarrow A_g (5.64 \text{ eV}) \) transition in CCB1. Frequencies of degenerate photons (\( \omega = \sqrt{E_f - E_i} \)) are given in electron-volts. \( \sigma^{2PA} \) are given in GM. All other values are in a.u.

<table>
<thead>
<tr>
<th></th>
<th>PQM</th>
<th>CCB1</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega )</td>
<td>2.82</td>
<td>1.27</td>
</tr>
<tr>
<td>( \sigma^{2PA} )</td>
<td>8453</td>
<td>6259</td>
</tr>
<tr>
<td>( \sigma^{2PA} )</td>
<td>98</td>
<td>15</td>
</tr>
<tr>
<td>( M_{xx}^{(i,j)} )</td>
<td>194.2</td>
<td>181.2</td>
</tr>
<tr>
<td>( M_{xx}^{(i,j)} )</td>
<td>10.1</td>
<td>13.3</td>
</tr>
<tr>
<td>( M_{xx}^{(i,j)} )</td>
<td>212.5</td>
<td>4.9</td>
</tr>
<tr>
<td>( M_{xx}^{(i,j)} )</td>
<td>3.8</td>
<td>183.3</td>
</tr>
<tr>
<td>( M_{xx}^{(i,j)} )</td>
<td>11.2</td>
<td>13.1</td>
</tr>
<tr>
<td>( M_{xx}^{(i,j)} )</td>
<td>4.2</td>
<td></td>
</tr>
</tbody>
</table>

with degenerate photons for the CSS1 \( \rightarrow A_g (5.64 \text{ eV}) \) transition is given in Table VIII. This cross section is larger than the cross section for the transition between the two lowest closed-shell singlet states in MX. Similar to MX, this transition features large 2PA transition moments, \( M_{xx} \), which are dominated by a single term involving the OSS state in the few-states model shown in Fig. 11. However, unlike the case of MX, a large \( M_{xx} \) value is a consequence of larger transition dipole moments (due to the longer distance between the radical centers and smaller \( \lambda \)) of both the initial and final states with the OSS state, even though the difference in the photon energy and the energy gap between the CSS1 and OSS states is relatively large.
For CCB1, the macroscopic 2PA cross section with degenerate photons for the CSS1 → A_1(2.54 eV) transition is given in Table VIII. The magnitude is comparable to the 2PA cross section for the CSS1 → A_1(5.64 eV) transition in PQM. Note that the increase in the diradical character in CCB1 relative to PQM is countered by the increase in the distance between the carbon centers.

V. CONCLUSIONS

We presented static polarizabilities and 2PA cross sections calculated with the EOM-SF-CCSD method for the few lowest electronic states of prototypical diradicals such as benzenes, m-didehydroxylenes, and p-quinodimethane and its extended analogue. For these nonlinear properties, we constructed few-states models in order to analyze the trends across different electronic states. We find that the static polarizabilities of the open-shell singlet states in these diradicals are larger than that of the lowest triplet and closed-shell singlet states. Using the few-states models, we explained this trend in terms of the larger transition dipoles and smaller energy gaps of the open-shell singlet states with the second closed-shell singlet states. The 2PA cross sections with degenerate photons are larger for the fully symmetric transitions between the closed-shell singlet states, in comparison to the transitions between the lowest closed-shell and open-shell singlet states. This is due to the large transition dipole moments of the open-shell singlet with the two closed-shell singlet states in the dominant sum-over-states terms for the symmetric transitions. We note that the macroscopic 2PA cross sections are small due to small values of the respective transition energies. We explained the trends in the relevant transition dipole moments between the open-shell singlet and closed-shell singlet states using a Hückel-type model, which allow us to derive structure-property relationships for these nonlinear properties in terms of the diradical character and the distance between the radical centers. In particular, we observe that in m-didehydroxylenes, the static polarizabilities of the lowest closed-shell singlet states increase while that of the open-shell singlet states decrease with decreasing diradical character. The 2PA cross sections for the fully symmetric transitions increase with decreasing diradical character and increasing distances between the radical centers, however, MX2 shows the largest 2PA cross section due to near-resonance enhancement. We further validated the trends in these properties and their dependence on the diradical character and the distance between the radical centers using PQM and CCB1 diradicals. Along with a qualitative measure of the diradical character computed using the leading EOM amplitudes, we also employed wave-function-analysis tools to calculate Head-Gordon’s index, which provides a robust measure of the diradical character.

SUPPLEMENTARY MATERIAL

See supplementary material for more details about the electronic states used in the few-states models and Cartesian geometries used in the calculations.

ACKNOWLEDGMENTS

A.I.K. acknowledges support by the U.S. National Science Foundation (No. CHE-1566428). We thank Dr. Marc de Wergifosse for his helpful comments on the manuscript.


The diradical “closed-shell singlet” state is not really a closed-shell state, but we use this terminology for convenience purposes.


