Ab initio and first principles theoretical investigations of triplet–triplet fluorescence in trimethylenemethane biradicals†

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Theoretical studies on triplet–triplet (T1 → T0) fluorescence of the arylated trimethylenemethane (TMM) biradicals, 32′′, were carried out using post-Hartree–Fock ab initio and various first principles density functional theory methods. Analysis of optimized geometries including bond alternations and spin distributions indicates that the triplet ground (32′′) and excited (32′′*) states of these biradicals have aromatic and quinoidal characteristics, respectively. Inspection of their calculated electronic structures shows that, in comparison to 32′′, one of the spins in 32′′* is more delocalized onto arene-rings linked to the TMM framework.

The trimethylenemethane (TMM, Fig. 1) biradical is a representative non-Kekulé molecule that has a triplet ground state (T0) owing to its D3h symmetry and pair of degenerate singly-occupied molecular orbitals (SOMOs). As a result of this characteristic, many theoretical and experimental studies have been carried out probing the curious electronic structures and magnetic properties of TMM biradicals.† The fact that these biradicals emit triplet–triplet (T1 → T0) fluorescence has received great attention.‡‡

In previous studies, Matsui, Ikeda, and coworkers described the observation of T1 → T0 fluorescence from the excited states of the 1-methyl-1-phenyl-, 1,1-diphenyl-, and 1-(2-naphthyl)-1-phenyl-substituted TMM biradicals, 32a–c* (Scheme 1). For this purpose, thermoluminescence (TL)‡‡ and two-color two-laser flash photolysis measurements were conducted using the corresponding aryl-substituted methylene-cyclopropanes 1a–c.‡‡ Moreover, T1 → T0 fluorescence of these biradicals was utilized as the basis for the design of a new organic light-emitting diode, termed “organic radical light-emitting diode.”‡‡

The electronic configurations of the excited T1 states of the TMM biradicals are complicated by their multi-conformation character. Additionally, electronic transition wavelengths and T0 geometries of compound 32b, computed using time-dependent (TD) density functional theory (DFT)§ with the B3LYP/cc-pVDZ method, are considerably different from the absorption and emission wavelengths observed experimentally.¶ Thus, more accurate and rigorous ab initio quantum chemical studies, and a detailed analysis of geometry relaxation occurring in the T1 state are required to have a greater understanding of the electronic structures of the excited states of TMM biradicals.

In the investigation described below, we carried out a theoretical study of the triplet–triplet fluorescence mechanism to accurately predict structural, electronic and T1 → T0 emission properties of triplet aryl-substituted trimethylenemethane biradicals 32′′*. Ab initio post-Hartree–Fock methods and three

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![Fig. 1](Image)

Fig. 1 (Top) Frontier molecular orbitals of the parent TMM biradical and (bottom) its corresponding Lewis resonance structures.
different (TD-)DFT functionals were used for this purpose. When treating open-shell systems, DFT methods often suffer from spin contamination, which usually is more severe when excited rather than ground states are computed. To validate the (TD-)DFT results, high-level \textit{ab initio} benchmark calculations where carried out on \(^2\Sigma^+\) and the calculated spin densities and excitation energies obtained by using both types of methods were compared. In this effort, the triplet excited states of three model aryl-substituted TMM biradicals were theoretically studied because they each emit one of the three primary colors (blue, green, and red) (Scheme 1).

All (TD-)DFT geometry optimizations were performed using the spin-unrestricted UB3LYP, UM06-2X, and CAM-UB3LYP functionals\(^*\) in conjunction with the 6-31G(d) basis set.\(^*\) (TD-)DFT single point energies were obtained using the same methods, however, the larger 6-311+G(d)\(^*\) basis set was employed. For the smallest, methyl-phenyl substituted biradical, \(^3\text{2a}'\), complete \textit{ab initio} active space self-consistent field (CASSCF)\(^*\) single point energy calculations with 10 \(\pi\)-orbitals and 10 electrons were performed, followed by a multi-reference second-order M\AE{}ller–Plesset perturbation (MRMP2) treatment.\(^*\) All DFT calculations were conducted using Gaussian 09,\(^*\) while the GAMESS-US\(^*\) and MOLPRO\(^*\) program packages were employed for the post-Hartree–Fock calculations. Below, we will refer to \(T_1\) and \(T_0\) states of \(^2\Sigma^+\) simply as \(^2\Sigma^+\) and \(^2\Sigma^+\), respectively.

In the first phase of this study, molecular geometry optimizations were carried out on \(^3\text{2a}'\) and \(^3\text{2a}'\) using various DFT functionals.\(^*\) The geometries of triplet ground (\(T_0\)) and excited (\(T_1\)) states of these biradicals, obtained by using UB3LYP/6-31G(d), are displayed in Fig. 2, and selected bond lengths are listed in Table 1. The lengths of the C5–C6, C6–C7 and C7–C8 bonds (see Fig. 2 for atom numbering) for \(^3\text{2a}'\) are in the range of 1.39–1.42 \(\text{\AA}\), which is typical for benzene-rings having a small degree of bond alternation. The results of applying a simulated harmonic oscillator model of the aromaticity (HOMA)\(^*\) of the phenyl group in \(^3\text{2a}'\) (0.927) suggests that its aromaticity is relatively high (\textit{i.e.}, roughly equal to that of benzene). In contrast, the respective C5–C6, C6–C7 and C7–C8 bond lengths in \(^3\text{2a}'\) are 1.47, 1.37, and 1.44 \(\text{\AA}\), suggesting that the degree of bond alternation is higher than in the ground state and, as a result, that the aromatic character of the phenyl group is reduced upon excitation to the \(T_1\) state. The greatly lower HOMA value (0.187) calculated for the phenyl group of \(^3\text{2a}'\) also indicates that its aromaticity is strongly reduced.

The changes in the C-C bond lengths taking place in proceeding from the diphenyl-substituted TMM biradical, \(^2\text{b}'\), to \(^3\text{2b}'\) are similar but somewhat less pronounced in comparison to those seen for the \(^3\text{2a}'\) system (Table 1). The calculated HOMA value changes are in accord with the reduction of aromaticity taking place in the phenyl group of \(^3\text{2a}'\) upon electronic excitation, with the largest change occurring in the monophenyl-substituted TMM biradical \(^2\text{a}'\). On the other hand, the calculated bond lengths and HOMA values for \(^3\text{2c}'\) and \(^3\text{2c}'\) deviate from this trend. In this case, the degree of aromaticity of the single phenyl group is less affected by excitation, presumably because excitation is localized mainly in the larger \(\pi\)-conjugated naphthyl group. The calculated dihedral angles composed of C1–C3–C4–C5 (yellow, Fig. 2) and C3–C4–C5–C6 (green) for the \(^2\Sigma^+\) system also follow these trends.

An analysis of their electronic structures provides further information about the nature of the excited TMM biradicals \(^2\Sigma^+\). Spin distributions of \(^3\text{2a}'\) and \(^3\text{2a}'\) at Franck–Condon regions are shown in Scheme 1. The calculated HOMA value (0.927) calculated for the phenyl group of \(^3\text{2a}'\) also indicates that its aromaticity is strongly reduced.

\begin{table}[h]
\centering
\begin{tabular}{lcccccc}
\hline
\textbf{Biradicals} & \textbf{C3–C4} & \textbf{C4–C5} & \textbf{C5–C6} & \textbf{C6–C7} & \textbf{C7–C8} & \textbf{HOMA}\(^*\) \\
\hline
\textbf{\(^3\text{2a}'\)} & 1.45 & 1.46 & 1.42 & 1.39 & 1.40 & 0.927 \\
\textbf{\(^3\text{2a}'\)} & 1.44 & 1.44 & 1.47 & 1.37 & 1.44 & 0.187 \\
\textbf{\(^3\text{2b}'\)} & 1.47 & 1.47 & 1.42 & 1.39 & 1.40 & 0.929 \\
\textbf{\(^3\text{2b}'\)} & 1.49 & 1.43 & 1.45 & 1.37 & 1.42 & 0.583 \\
\textbf{\(^3\text{2c}'\)} & 1.47 & 1.47 & 1.42 & 1.39 & 1.40 & 0.931 \\
\textbf{\(^3\text{2c}'\)} & 1.47 & 1.45 & 1.39 & 1.42 & 1.40 & 0.896 \\
\hline
\end{tabular}
\caption{Geometry parameters of \(^3\text{2a}'\) and \(^3\text{2a}'\) Obtained by using (TD-)UB3LYP/6-31G(d)}
\end{table}
Condon geometries were determined at the (TD)-UB3LYP/6-31G* level of theory (Fig. 3a). The results show that the spin densities of both 32a•• and 32b•• are almost completely localized at C4 (benzylic), C1 (allylic), and C2 (allylic). For 32a•–c•, the spin densities at C1 and C2 are almost identical to those of the corresponding ground state, 32a••. In contrast, the spin density at C4 of 32a•• is located close to the ipso-position (C5) of the phenyl group. The change taking place in spin densities at each atom in the 32b•• → 32b•• transition is similar to those occurring in the 32a•• → 32a•• transition. Interestingly, the spin density changes caused by the 32c•• → 32c•• transition occur most prominently in the 2-naphthyl group. The alterations in electronic structure are consistent with the geometrical changes that take place in all of the 32•• → 32•• transitions (see the discussion in the previous section).

To express the spin distribution changes that take place in 32•• → 32•• transitions in a quantitative manner, we express the difference in the spin density of the ith atom, \( N_{i}^{T_{1}-T_{0}} \) by the equation given in eqn (1),

\[
N_{i}^{T_{1}-T_{0}} = (\alpha_{i}^{T_{1}} - \beta_{i}^{T_{1}}) - (\alpha_{i}^{T_{0}} - \beta_{i}^{T_{0}})
\]

where \( \alpha_{i}^{T_{1}/T_{0}} \) and \( \beta_{i}^{T_{1}/T_{0}} \) are the respective natural spin densities estimated from \( \alpha \) and \( \beta \) natural orbitals for \( 32a•\) and \( 32a•\) (see Tables S7–S9†). Inspection of the data listed in Fig. 3a shows that the spin distributions at C1, C2, and C3 (the allyl moiety) do not significantly change during the \( 32a•\) → \( 32a•\) transition. Moreover, the sum of their spin densities is approximately 1.1 each for \( 32a•\) and \( 32a•\) (see Table S10†). Thus, it appears that one unpaired electron is delocalized over the allyl moieties of both \( 32a•\) and \( 32a•\). The other unpaired electron in the T1 exited state \( (32b••)\) is delocalized over the remainder of the molecule, whereas it is localized on C4 in \( 32a•\). The electronic structure change occurring upon excitation is also made apparent by inspection of the flow of spin density from C4 to C5 (Fig. 3b). The excitation-promoted, spin density reorganization decreases on proceeding from \( 32a•\) to \( 32c•\). In addition, introduction of benzene or naphthalene rings leads to an enhancement in electron delocalization in the T0 state (Tables S7–S9†). The analysis presented above indicates that electronic structures of \( 32a•\) and \( 32a•\) can be schematically depicted in the manner shown in Scheme 1. As a result, the distribution of the second unpaired electron is controlled by introduction of aromatic groups on the TMM biradical backbone (e.g., \( 32c•\)).

Previously, Ikeda and co-workers experimentally determined the wavelength maxima for \( T_{1} \rightarrow T_{0} \) fluorescence of \( 32b•• \) by using TL methods.\(^{24}\) The TL maxima of \( 32a••, 32b•• \) and \( 32c•• \) in methylecyclohexane matrices at ca. 130 K are 451, 501, and 602 nm, respectively. In the present work, we calculated the fluorescence wavelengths of \( 32a••, 32b•• \) using various TD-DFT functionals (Table 2). Interestingly, the fluorescence wavelengths obtained by using the UB3LYP method match well with the experimentally determined values.\(^{25}\) Although use of the UM06-2X method also gives maxima that are close to the experimental values, it slightly overestimates the excitation energies. Utilization of the long-range corrected CAM-UB3LYP functional does not lead to improved results, suggesting that charge-transfer interactions are not important in \( 32b•• \). The use of UHF in this functional for treatment of large electronic separations suffers from a more serious spin contamination (\( \langle S^{2} \rangle \sim 2.54-4.01 \)), especially in the case of \( 32c•• \).

| Table 2 | Fluorescence wavelength maxima \( \lambda_{\text{em}} \) and oscillator strengths \( f \) of TMM biradicals obtained by experimental and various TD-DFT methods |
|--------|-------------------|-------------------|-------------------|-------------------|
|        | \( \lambda_{\text{em}}/\text{nm} \) | \( \lambda_{\text{em}}/\text{nm} \) \( \langle S^{2} \rangle, f \) | \( \lambda_{\text{em}}/\text{nm} \) \( \langle S^{2} \rangle, f \) | \( \lambda_{\text{em}}/\text{nm} \) \( \langle S^{2} \rangle, f \) |
|        | TL                | UB3LYP            | UM06-2X           | CAM-UB3LYP        |
| 32a••  | 451               | 443 (2.43, 0.003) | 438 (2.28, 0.005) | 440 (3.10, 0.001) |
| 32b••  | 501               | 479 (2.24, 0.010) | 464 (2.23, 0.018) | 443 (2.54, 0.007) |
| 32c••  | 602               | 613 (2.63, 0.002) | 554 (2.39, 0.004) | 903 (4.01, 0.000) |

\(^{a}\) From ref. 5a. \(^{b}\) The 6-311+G(d) and 6-31G(d) basis sets were employed for single point calculations and optimizations, respectively.
To validate the (TD)-DFT results presented above, the electronic configuration of $2a^{-*}$ was evaluated by employing post-Hartree–Fock CASSCF and multireference MP2 calculations. First, 10 $\pi$-orbitals of $2a^{-*}$ were obtained using the RHF/6-311+G(d) method for the singlet spin state. Subsequent CASSCF calculations were carried out using a full $\pi$-orbital (10e, 10o) active space for the triplet ground state. In Table 3 are listed the corresponding natural orbital occupation numbers (NOON), where 2, 1, and 0 indicates doubly-, singly-, and un-occupied orbitals, respectively. Importantly, a deviation of NOON from integer numbers implies that the wavefunction has multireference character. Analysis of the NOON values for $2a^{-*}$ indicates the existence of four doubly-occupied (NOON > 1.87), two singly-occupied (NOON ≈ 1.00), and four un-occupied (NOON < 0.13) orbitals within the active space. On the other hand, the NOON values of orbitals numbers 4 and 7 in $2a^{--*}$ deviate largely from integer values, signaling that the wavefunction has multireference character. Except for natural orbitals 4–7, the NOON values and orbital shapes of $32a^{**}$ and $32a^{-*}$ are almost identical. The singly-occupied natural orbital of $2a^{-*}$ is localized on the TMM moiety, while singly occupied natural orbitals of $2a^{**}$ (Table 3) are delocalized on the phenyl group. The fact that this finding is consistent with the natural charge distributions obtained by using (TD-)DFT calculations (Fig. 3) validates the DFT-based results.

The CASSCF-determined emission energy of the benchmark model $32a^{**}$ is 2.62 eV (473 nm) and that arising from MRMP2 is 2.51 eV (495 nm). The MRMP2 result is in good agreement with that determined experimentally (2.74 eV, 451 nm), and the TD-DFT determined emission energy (2.82 eV, 440 nm) is also close to the experimental value. These findings suggest that a well-balanced use of dynamic and non-dynamic correlations is necessary for quantitatively accurate assessment of the emission wavelengths of $32^-*$. The somewhat surprising similarity of the MRMP2 and UB3LYP results show that conceptually more simple density functional approaches can be applied to the complex electronic and molecular structures of $32^-*$. This is most likely a consequence of fortuitous error compensations.

In conclusion, studies aimed at understanding the T1 $\rightarrow$ T0 fluorescence of aryl-substituted TMM biradicals $32^-**$ were carried out using quantum chemical calculations. The results of calculations using high-level ab initio and various DFT functionals reveal that the wavefunctions of $32^-**$ possesses significant multireference character. However, use of DFT approaches with sufficiently large basis sets leads to predictions of reasonable emission wavelengths of $32^-*$. In addition, the calculated changes of bond lengths and spin distributions demonstrate that significant relaxation of molecular geometries occurs in T1, on going from an aromatic ground state to quinoid structured excited state. The overall results of this work demonstrate that it is possible to use DFT-based methods to estimate accurately the fluorescence properties of organic open-shell species. This ability should accelerate the development and application of luminescent radical materials.

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