A comparative multi-reference configuration interaction study of the low-lying states of two thione isomers of thiophenol

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Abstract
Multi-reference configuration interaction, MR-CI (including extensivity corrections, named +Q), calculations were performed on the S0–S3 states of cyclohexa-2,4-diene-1-thione (thione 24) and cyclohexa-2,5-diene-1-thione (thione 25), which are thione isomers of thiophenol. Several types of uncontracted MR-CIS and MR-CISD wavefunctions were employed, comprising MR-CI expansions as large as \( /C24 365 \times 10^6 \) configuration state functions. The nature of the studied excited states was characterized. Vertical excitation energies (ΔE) and oscillator strengths (f) were computed. The most intense transitions (S0 → S2 for 24 and S0 → S3 for 25) do not change with the wavefunction, although a variation as large as ~1 eV was obtained for the S3 state of 24, at the highest (MR-CI+Q) level. On the other hand, ΔE changes at most by ~0.56 eV for 25 as the wavefunction changes, at the same level. The S1 state of both thiones was found to have nπ* character and is in the visible region. For 24, S2 and S3 are ππ* and nπ* states, respectively, while for 25 the reverse order is obtained. S2 and S3 are in the range ~3.5 to 5.2 eV, again at the highest level. It is the first time that the excited states of the title molecules are studied. The computed results agree with the experimental onset of photoreactions of thiones 24 and 25 found by Reva et al (Phys. Chem. Chem. Phys., 2015, 17, 4888).

KEYWORDS
excited states, multi-reference configuration interaction, thione isomers of thiophenol

1 | INTRODUCTION

Cyclohexa-2,4-diene-1-thione (24; Figure 1) has been identified in a ground-state isomerization reaction of thiophenol, studied at the MP2 and QCISD(T) levels by Al-Muhtaseb et al.[1] Those authors obtained a very large barrier of ~63 kcal mol\(^{-1}\) for the thiophenol → 24 thiol–thione H-transfer reaction. Although the formation of the analogous cyclohexa-2,5-diene-1-thione (25; see Figure 1) was also studied, the authors did not find a direct pathway for the formation of 25 from thiophenol.[1]

Reva et al[2] isolated thiophenol in cryogenic argon matrices and observed the reversible photochemical thiophenol → 24 and 24 → 25 reactions. This was the first experimental observation of the thione isomers 24 and 25. According to the authors, the direct thiophenol → 25 photoisomerization reaction could neither be discarded nor confirmed.[2]

In the present work, the first three excited singlet states of 24 and 25 were studied at the MR-CIS and MR-CISD levels, with the inclusion of extensivity corrections (hereafter named +Q). Basis set effects were also taken into account. The results obtained for the two investigated
systems were then used to address the excited states reached in the photochemical experiments by Reva et al.[2] This is the first time that the excited states of thiones 24 and 25 are studied.

2 | COMPUTATIONAL METHODS

The optimized structures of molecules 24 and 25 were taken from Reva et al.[2] (B3LYP/aug-cc-pVTZ data). Frequency calculations were also performed by the same authors[2], confirming that the obtained structures correspond to minima. Molecules 24 and 25 have Cs and C2v symmetry, respectively.

In the present study, the active space used for thiones 24 and 25 at the CASSCF level (state average calculations) consists of 12 electrons in 11 orbitals. Two A' and two A' states were averaged at the CASSCF level for 24, while for 25 one state for each one of the four symmetries (A2, B2, B3, and A1) was averaged (in both cases with the same weights). For both systems, these are the four lowest states at the CASSCF level. Because of the equivalence between the two Cs H bonds of 24 and 25, the σ orbitals in these molecules are equally localized on these bonds. Two pairs of active σ orbitals, namely the σCS/σC-H and σCS/σCS pairs, were included for both 24 and 25. The C atom of the former pair is the sp^3 C atom, for both molecules (Figure 1).

For 25, three of the six active σ orbitals are named σCS + σring (≡ σ1), nS (≡ σ3), an essentially nonbonding S orbital, and σC-C (≡ σ2, mainly localized on the C=C bonds, named σ2). The other nonbonding S orbital, perpendicular to the previous one, is simply named n, and the three antibonding σ orbitals are named σ^*CS + σ^*ring (≡ σ4), σ^*C-C (≡ σ5), and σ^*ring (≡ σ6).

For 24, a nonbonding S orbital is again named n (as for 25). The three bonding active σ orbitals are named σ1, σCS (≡ σ2), and σ5 + σC-C (≡ σ3), while the antibonding orbitals are named σ^*1, σ^*CS (≡ σ4), σ^*ring + σ^*CS (≡ σ5), and σ^*C-C (≡ σ6).

The subscripts of the orbitals (such as CS, C-C, etc.) refer to their localization. Additional details can be found in Supporting Information.

The σCS/σCS pairs of 24 and 25 were included in the active space (for most of the wavefunctions here used), as this study is the first step towards a description (on the same grounds) of photoinduced hydrogen migration pathways associated with the thiophenol → 24, thiophenol → 25, and 24 → 25 reactions. Besides, the above-mentioned active space was constructed considering also the following two reasons: (a) As some preliminary calculations at the CASSCF level performed for thiophenol showed that the σCS/σCS pair should be included in the active space because of its admixture with the σSH/σSH pair, the former pair was also included in the active spaces of 24 and 25 (for most of the wavefunctions here used), due to the thiophenol → 24 and thiophenol → 25 reactions[2] which we intend to study. (b) The highest level results for thiophenol (at the CASPT2 level, discussed later and compared to the results here obtained) include the 11 orbitals which transform into the 11 orbitals here used for 24 and 25, along the thiophenol → 24 and thiophenol → 25 reaction pathways (as will be discussed elsewhere).

Five types of wavefunctions were used in this work, named w1, w1', w2, w3, and w4. w1 and w1' are MR-CIS wavefunctions, while the remaining are MR-CISD wavefunctions. w1, w1', and w4 are used for both systems, whereas w2 is only used for 25. For w2, the CAS space has been reduced, transferring strongly and weakly occupied orbitals to the doubly occupied (DOCC) and auxiliary (AUX) spaces, respectively, as discussed below. w1' is derived from w2 simply by reducing the internal → external excitation level from singles and doubles to singles only (Table 1). For w3, the CAS orbitals are split into reduced active space (RAS) and AUX orbitals. It was not possible to use w3 for 25, as in this case single occupied → antibonding excitations are not enough to generate the correct number of guess vectors for each irreducible representation. In the case of w4, the four σ orbitals have been removed from the CAS (at both CASSCF and MR-CI levels), and the n and σ1 orbitals (24a/9b2 and 3a'/3b1, respectively, see Supporting Information) have been transferred to the RAS space, and only single RAS → CAS excitations are allowed while generating the reference configuration state functions (CSFs), yielding a set of reference CSFs based on a CAS(4,5) + single RAS → CAS excitations. Additional details concerning how these four wavefunctions are formed are given in Table 1.

FIGURE 1 Thione isomers of thiophenol: cyclohexa-2,4-diene-1-thione (24, reads: “two-four”) and cyclohexa-2,5-diene-1-thione (25, reads “two-five”)
TABLE 1  Wavefunctions used in this work at the MR-CI level

<table>
<thead>
<tr>
<th>Wavefunction</th>
<th>Excitation levels used to generate the reference CSFs(^a)</th>
<th>Internal → external(^b) excitation level/final MR-CI wavefunction</th>
</tr>
</thead>
<tbody>
<tr>
<td>w1</td>
<td>CAS(12,11)</td>
<td>Singles/MR-CIS</td>
</tr>
<tr>
<td>w1'</td>
<td>CAS(8,6) + single CAS → AUX excitations</td>
<td>Singles/MR-CIS</td>
</tr>
<tr>
<td>w2</td>
<td>CAS(8,6) + single CAS → AUX excitations</td>
<td>Singles and doubles/MR-CIS</td>
</tr>
<tr>
<td>w3(^c)</td>
<td>single occ → anti-bonding excitations</td>
<td>Singles and doubles/MR-CIS</td>
</tr>
<tr>
<td>w4</td>
<td>CAS(4,5) + single RAS → CAS excitations</td>
<td>Singles and doubles/MR-CIS</td>
</tr>
</tbody>
</table>

\(^a\)Configuration state functions.
\(^b\)Internal corresponds to the set of doubly occupied + active + AUX orbitals, while external corresponds to the set of orbitals that are unoccupied (virtual) in the reference CSFs.
\(^c\)For w3, occ comprises the subset of six orbitals (active at the CASSCF level) with the highest occupation numbers, while the antibonding subset comprises the five active orbitals with the smallest occupation numbers. For additional details concerning these orbitals, see text and Supporting Information.

w2 is the largest MR-CISD wavefunction here used (Table 1) and has only been employed for 25 because of its higher \(C_{2v}\) symmetry (Figure 1), but at the expense of a reduced number of active orbitals. This reduction consists of transferring the former active orbitals, namely two bonding (\(\sigma_{CS}\) and \(\sigma_{CI}\)) and three antibonding orbitals (\(\sigma_{CS}^*\), \(\sigma_{CH}^*\), and \(\sigma_{\text{ring}}^*\); see Supporting Information) to the DOCC and AUX spaces, respectively, at the MR-CISD level.

The criteria chosen for these two sets of w2 were as follows: the active orbitals whose occupation numbers (nocc) are (at the CASSCF level) larger than 1.97 were transferred to the DOCC space, while those with nocc < 0.1 were transferred to the AUX space, and only single CAS→AUX excitations were allowed (yielding a set of reference CSFs based on a CAS(8,6) + single CAS→AUX excitations, see Table 1). One can check the importance of double internal → external excitations through a comparison between the results obtained from w1' and w2. On the other hand, a comparison between w1 and w1' allows checking the effect of the reference wavefunction on the relative accuracy of the MR-CIS wavefunctions.

Because of the size of the system and the basis sets used, multi-reference configuration interaction calculations with single and double excitations (MR-CISD) are feasible only for 24 with a large reduction of the number of reference CSFs, at least for uncontracted MR-CI wavefunctions (as discussed later). Such reduction was applied to yield the wavefunctions w3 and w4 (Table 1). The first one was devised with the purpose to see what the net effect of reducing the internal excitation level is (in other words, splitting the CAS into RAS + AUX orbitals) but at the same time increasing the internal → external excitation level, yielding an MR-CISD wavefunction. w3 has a size similar to that of w1. Again, because of the size of the system, an internal excitation level larger than 1 (between the occ and the antibonding subsets described in Table 1), combined with single and double internal → external excitations (yielding an MR-CISD wavefunction), is computationally prohibitive for 24. However, the relatively small number of active orbitals used in w4 allows all excitations compatible with a CAS(4,5). Besides, as explained before, additional reference CSFs are also generated through RAS → CAS excitations (Table 1). w4 corresponds to the largest CI expansion used for 24.

Once the reference CSFs were formed, they were used to generate the excited CSF through single excitations from all internal into all external orbitals, at the MR-CIS level (for w1 and w1', see Table 1), and through single and double internal → external excitations at the MR-CISD level (for w2, w3, and w4, see Table 1). The final CSF space is formed by the reference along with the excited CSFs.

There are two subsets of low-lying orbitals at the ground-state geometries, namely the frozen core (FC) and the doubly occupied valence orbitals, at the MR-CIS/MR-CISD levels. The FC subset comprises the K (for the C atom) and K + L (for the S atom) shells. Such choice for the FC is based on the essentially correct description of the excited states of other systems containing another third-row atom, Cl, at the MR-CISD level. The difference between doubly occupied and FC orbitals is that, while the former set remains doubly occupied only in the reference CSFs, the latter is kept as such in the reference and the excited CSF space. The multireference extension of the Davidson correction (+Q) was used to take the size-extensivity error into account.21–23 Rigorously speaking, the Davidson correction should be used only for CISD/MR-CISD wavefunctions, but not for CIS/MR-CIS wavefunctions.22 According to eqs (42) and (43) from Lischka et al.22 it is clear that the stabilization due to the Davidson correction is always larger for an MR-CISD wavefunction, as compared to that for an MR-CIS wavefunction formed from the same set of reference CSFs. This is due to (a) the sum of the weights of the reference CSFs is always smaller in the MR-CISD than in the MR-CIS wavefunction, and (b) the final MR-CISD energy is always smaller than the final MR-CIS energy. Thus, as the final MR-CISD energy is always smaller than the final MR-CIS energy, the Davidson-corrected MR-CISD energy is always smaller than the Davidson-corrected MR-CIS energy.

However, error cancellation effects can lead to similar Davidson corrections for the excitation energies computed with MR-CIS and MR-CISD wavefunctions (which is the case for the w2 and w1' calculations performed for 25, as discussed later). As such error cancellation effects are not guaranteed, one should be cautious while using the Davidson correction formula for MR-CIS wavefunctions.

The interactive space restriction24 was used for w2 and w4 (Table 1). All CASSCF, MR-CISD, and MR-CISD + Q calculations were performed with the COLUMBUS program system.15–18 The atomic orbital (AO) integrals used by COLUMBUS were computed with the DALTON program.19 The aug-cc-pVTZ and the mixed aug-cc-pVDZ(C,H)/aug-cc-pVTZ(S) basis sets were used in this study.20–22
3 | RESULTS AND DISCUSSION

3.1 | Basis set effect

The basis set effect was taken into account at the CASSCF level for both systems (Table 2) and at the \(w_1\) and \(w_4\) levels for 25 (Table 3). As can be seen from Tables 2 and 3, the \(\Delta E\) values obtained with both basis sets differ by at most 0.03 eV. Besides, the main configurations obtained for all four states do not change with the basis set, and the differences between their weights are virtually negligible, at the CASSCF, \(w_1\), and \(w_4\) levels. Besides, the differences between the \(f\) values obtained with the two basis sets are small at the \(w_1\) and \(w_4\) levels (Table 3). Therefore, the results shown in Tables 2 and 3 give us confidence about the reliability of the aug-cc-pVDZ(C,H)/aug-cc-pVTZ(S) basis set with respect to the computationally more demanding aug-cc-pVTZ(C,H,S) basis set.

3.2 | Vertically excited states of 24 and 25

The \(\Delta E\) values, configuration weights, and oscillator strengths \((f)\) computed with \(w_1\), \(w_2\), \(w_1^*\), and \(w_4\) for 25 are shown in Table 3. As can be seen through comparison between Tables 2 and 3, inclusion of dynamic electron correlation (at both MR-CIS and MR-CISD levels) changes the \(\Delta E\) values by at most 0.41 eV. A decrease in the \(\Delta E\) values is obtained upon inclusion of extensivity correction, but the effect is smaller than that of the dynamic electron correlation, leading to a maximum change of 0.19 eV. The nature of all studied states is the same at the CASSCF and MR-CI levels (compare Tables 2 and 3). It is important to point out the non-negligible contribution of configurations formed by double excitations to the \(n_1^*\) orbital in the \(1^1B_1\) and \(1^2B_2\) states, although these weights decrease upon inclusion of dynamic electron correlation (compare Tables 2 and 3).

An important difference between the results obtained for thione isomers 24 and 25 and those obtained for the thiol isomer (thiophenol) is the absence of configurations formed by excitations to the \(\sigma\) orbital, a feature observed for the \(S_2\) state of thiophenol.\(^{23-27}\) However, such difference is expected, as in thiophenol this orbital is localized on a considerably weaker (S–H) bond.

Using the CASPT2/aug-cc-pVTZ results for thiophenol as ref.\(^ {23}\) (4.3, 4.5, and 5.1 eV for the \(S_1\), \(S_2\) and \(S_3\) states, respectively), one can see a decrease in the excitation energies (as one goes from thiophenol to 25), with the largest effect obtained for the first excited state, followed by the second excited state. Compared to the highest level \(w2(+Q)\) results (as discussed later), the decrease for \(S_1\) is as large as \(\sim 2.1\) eV, while for \(S_2\) one sees an increase of only \(\sim 0.3\) eV, at the same level. For \(S_3\), the changes are almost negligible, at both \(w2(+Q)\) and \(w4(+Q)\) levels. For \(w1\) and \(w1^*\), decreases of \(\sim 0.3\) eV are obtained (Table 3). It is important to stress that one should be cautious while comparing the results obtained with different molecules, as part of the difference is likely to be due to the methods. Nevertheless, as a much larger effect has been observed for \(S_1\), it is very likely that at least in this case the obtained trend is correct.

It is interesting to point out the change of nature of \(S_2\) of the thione isomer 25 as compared to the thiol form of thiophenol. Although there is some contribution of the \(n\) orbital (perpendicular to the \(x\) system of the ring) to the \(\sigma_{SH}\) and \(\sigma_{SC}\) orbitals of thiophenol,\(^ {24}\) configurations containing excitations from these orbitals are absent in the lowest four excited states of thiophenol.\(^ {23-27}\) On the other hand, in 25 (and also in 24, as discussed later) the \(n\) orbital is very well localized (as shown in Supporting Information). While in thiophenol \(S_1\) is a \(\pi^*\) state, in 25 it is an \(n\sigma^*\) state. As \(S_2\) is also an \(n\pi^*\) state, and \(S_3\) is a \(\pi\pi^*\) state (Table 3). Thus, only the nature of \(S_3\) is the same both in thiophenol\(^ {23}\) and in the thione isomer 25.

The first excited state of 25 (11A2) is in the visible region (with \(\Delta E = 2.15\) or 2.36 eV, at the \(w2(+Q)\) and \(w4(+Q)\) levels, respectively), but the 11A2 \(\rightarrow 1^1A_2\) transition is dipole-forbidden, by symmetry. However, the experimental threshold required for photochemical transformations of 25, \(\lambda < 332\) nm (3.73 eV), is consistent with a transition within the first band (Table 3). Therefore, some intensity gain is expected to be taking

| TABLE 2 | \(\Delta E\) values (in eV) and configuration weights computed at the CASSCF level with the aug-cc-pVDZ(C,H)/aug-cc-pVTZ(S) basis set, for 24 and 25 thione isomers |
|---|---|---|---|---|---|---|---|
| State | \(\Delta E\) | Configurations\(^{ab}\) | State | \(\Delta E\) | Configurations\(^{ab}\) |
| 11A' | 0.00 | 0.60g^s + 0.25n^s1^* | 11A1 | 0.00 | 0.75g^s + 0.10n^s1^* |
| 11A'' | 2.09 (2.07)^c | 0.80n^s1^* | 11A2 | 2.18 (2.16)^c | 0.83n^s1^* |
| 21A' | 4.50 (4.49)^c | 0.21x2^s1^* + 0.19x3^s1^* + 0.15x3^s0^1^* + 0.12x3^g^s2^* | 21B1 | 4.98 (4.95)^c | 0.45n^s2^* + 0.29x2^s2^* + 0.27x2^g^s1^* |
| 21A'' | 4.55 (4.53)^c | 0.44n^s2^* + 0.23nx3^s1^* + 0.12nx3^g^s1^* + 0.23nx2^s1^* | 21B2 | 5.36 (5.35)^c | 0.28n^s2^* + 0.27x2^g^s1^* + 0.19x2^s1^* |

\(^{a}\)gs stands for the ground-state configuration; only configurations with weights larger than 0.1 are shown.

\(^{b}\)Configurations \(a^b\) and \(a^b^c\) correspond to the \(a \rightarrow b\) and \((a,b) \rightarrow c\) double excitations, respectively, and the remaining configurations correspond to single excitations.

\(^{c}\)Results obtained with the aug-cc-pVTZ(C,H,S) basis set. The weights obtained with both basis sets differ by at most 0.01.
The nearby S0 Multi-reference extension of the size-extensivity Davidson correction is indicated by (+Q). Note: Can be considered a relatively good approximation to place around 3.73 eV, as a result of vibronic and/or spin–orbit coupling mechanisms. Besides, one cannot rule out some intensity borrowing from the nearby S0–S1 transition. Because of the judicious choice of the CASSCF active orbitals to be transferred to the DOCC and AUX spaces while forming the reference set of CSFs for w2 (Table 1 and the previous discussion concerning the criteria used for this transfer), it is expected that w2 already recovers a large fraction of the electron correlation of an MR-CISD wavefunction formed from a set of CAS(12,11) reference CSFs. Consequently, the results obtained with w2 can be considered the most reliable ones for 25. As already mentioned, w2 is the largest MR-CI wavefunction here employed, achieving 3.6 × 10⁶ CSFs. From what has been said, one can test the reliability of w1′ for 25 by comparing its results with those obtained from w2. Such comparison will allow addressing the importance of the double internal → external excitations (Table 1). As can be seen from Table 3, the computed excitation energies are close, with a maximum difference of 0.28 eV, obtained for 1¹B₂ including extensivity corrections. The main configurations are maintained for w1′ and w2, and the largest change obtained for the configuration weights is 0.14 (for 1¹B₁), a value which can be considered relatively small. On the other hand, the effect on the f values, due to the change from w1′ to w2, is significant, with reductions down to ~15% and 59% for 1¹B₁ and 1¹B₂, respectively (Table 3). Despite such reduction, the S₀ → S₂ transition remains the most intense one for both wavefunctions. Therefore, w1′ can be considered a relatively good approximation to w2 (a computationally much more demanding wavefunction). Besides, due to the error cancellation effects mentioned previously, the size-extensivity correction in the ΔE values computed with w1′ and w2 are similar (Table 3).
As can be seen from Table 3, the effect associated with the change from \( w_1 \) to \( w_1' \) is smaller than that between \( w_2 \) and \( w_1' \) for the \( \Delta E \) and \( f \) values. The \( \Delta E \) values change by at most 0.13 eV, and the \( f \) values increase by \( \sim 16\% \) and \( 29\% \) for the \( S_0 \rightarrow S_2 \) and \( S_0 \rightarrow S_3 \) transitions, respectively, while changing the wavefunction from \( w_1 \) to \( w_1' \). The main configurations remain the same, and their weights virtually do not change upon the change from \( w_1 \) to \( w_1' \) (Table 3).

Through a comparison between \( w_2 \) and \( w_4 \), one can verify how good the latter is as an approximation to the former. Without extensivity correction, the largest difference between the \( \Delta E \) values computed with \( w_2 \) and \( w_4 \) is 0.35 eV. Upon inclusion of extensivity correction, one has slightly smaller differences, of at most 0.24 eV. Interestingly, with or without extensivity correction the difference between the \( \Delta E \) values of \( S_1 \) obtained from \( w_2 \) or \( w_4 \) is virtually negligible (Table 3). As the wavefunction changes from \( w_2 \) to \( w_4 \), the \( f \) values increase only by \( \sim 15\% \) and \( 7\% \) for the \( S_0 \rightarrow S_2 \) and \( S_0 \rightarrow S_3 \) transitions, respectively. Again, the main configurations are maintained and their weights change by at most 0.05, from \( w_2 \) to \( w_4 \) (Table 3). Thus, \( w_4 \) can be considered a good approximation to \( w_2 \), especially if extensivity correction is included.

The \( \Delta E \) values, configuration weights, and oscillator strengths (f) computed with \( w_1, w_1', w_3, \) and \( w_4 \) for \( 24 \) are shown in Table 4. It is clear that the effect of dynamic electron correlation is considerably larger for the \( \Delta E \) values of \( 24 \) than for those of \( 25 \) (especially for \( S_2 \) and \( S_3 \)) and the effect for the latter is slightly dependent on the state (compare Table 2 with Tables 3 and 4). On the other hand, for \( 24 \) the effect of dynamic electron correlation is highly dependent on the state and on the wavefunction. For instance, as for the \( 2\bar{A}' (S_2) \) state computed with \( w_1 \), a reduction of 0.68 eV is obtained, while for the same state calculated with \( w_3 \) and \( w_4 \) one has reductions of only 0.24 and 0.19 eV, respectively, upon inclusion of dynamic electron correlation. However, in the case of the fourth state (\( 2\bar{A}'' \)) a much larger change is obtained for \( w_3 \) compared to that of \( w_1. \)

### Table 4

<table>
<thead>
<tr>
<th>States</th>
<th>( \Delta E )</th>
<th>( \Delta E + Q )</th>
<th>( f \times 10^3 )</th>
<th>Configurations (^a^b)</th>
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<tbody>
<tr>
<td>( 1\bar{A}' )</td>
<td>0.00</td>
<td>0.00</td>
<td>—</td>
<td>( 0.62 g_s + 0.19 \pi_3 \pi_1^* )</td>
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<tr>
<td>( 1\bar{A}'' )</td>
<td>1.92</td>
<td>1.88</td>
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<td>( 2\bar{A}' )</td>
<td>3.82</td>
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<td>4.32</td>
<td>4.22</td>
<td>0.061</td>
<td>( 0.52 n_2^* + 0.18 n_3 \pi_1^2 )</td>
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<table>
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<tr>
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<tbody>
<tr>
<td>( 1\bar{A}' )</td>
<td>0.00</td>
<td>0.00</td>
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<td>( 0.63 g_s + 0.19 \pi_3 \pi_1^* )</td>
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<tr>
<td>( 1\bar{A}'' )</td>
<td>1.95</td>
<td>1.96</td>
<td>0.052</td>
<td>( 0.81 n_1 )</td>
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<tr>
<td>( 2\bar{A}' )</td>
<td>3.88</td>
<td>3.56</td>
<td>293.0</td>
<td>( 0.57 \pi_3 \pi_1^* + 0.18 g_s )</td>
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<td>( 2\bar{A}'' )</td>
<td>4.38</td>
<td>4.31</td>
<td>0.073</td>
<td>( 0.51 n_2^* + 0.20 n_3 \pi_1^* )</td>
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<tr>
<td>( 1\bar{A}' )</td>
<td>0.00</td>
<td>0.00</td>
<td>—</td>
<td>( 0.61 g_s + 0.16 \pi_3 \pi_1^* )</td>
</tr>
<tr>
<td>( 1\bar{A}'' )</td>
<td>2.27</td>
<td>2.36</td>
<td>0.053</td>
<td>( 0.77 n_1 )</td>
</tr>
<tr>
<td>( 2\bar{A}' )</td>
<td>4.26</td>
<td>4.06</td>
<td>317.1</td>
<td>( 0.53 \pi_3 \pi_1^* + 0.13 g_s )</td>
</tr>
<tr>
<td>( 2\bar{A}'' )</td>
<td>5.47</td>
<td>5.25</td>
<td>0.033</td>
<td>( 0.76 n_2^* )</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>States</th>
<th>( \Delta E )</th>
<th>( \Delta E + Q )</th>
<th>( f \times 10^3 )</th>
<th>Configurations (^a^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1\bar{A}' )</td>
<td>0.00</td>
<td>0.00</td>
<td>—</td>
<td>( 0.56 g_s + 0.16 \pi_3 \pi_1^* )</td>
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<tr>
<td>( 1\bar{A}'' )</td>
<td>2.31</td>
<td>2.19</td>
<td>0.041</td>
<td>( 0.73 n_1 )</td>
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<tr>
<td>( 2\bar{A}' )</td>
<td>4.31</td>
<td>4.09</td>
<td>179.8</td>
<td>( 0.32 \pi_3 \pi_1^* + 0.13 n_2 \pi_1^* )</td>
</tr>
<tr>
<td>( 2\bar{A}'' )</td>
<td>4.83</td>
<td>4.62</td>
<td>0.001</td>
<td>( 0.46 n_2^* + 0.19 n_3 \pi_1^* )</td>
</tr>
</tbody>
</table>

Note: Multi-reference extension of the size-extensivity Davidson correction is indicated by \( (+Q) \).

\(^a\)gs stands for the ground-state configuration; only configurations with weights larger than 0.1 are shown.

\(^b\)Configurations \( a,b^1c^2 \) correspond to the \( (a,b) \) double excitations, while the remaining configurations correspond to single excitations. For \( w_1, w_1', w_3, \) and \( w_4 \) the total MR-CI/MR-CI+Q energies are (in au) –628.521163/–628.539777, –628.466399/–628.484396, –629.050072/–629.212969, and –629.073981/–629.225881, respectively.
obtained for w1 (0.92 vs 0.23 eV). In contrast, for w4 one has a slight increase of 0.28 eV (compare the CASSCF and MR-CI results from Tables 2 and 4, respectively).

Albeit the nature of the excited states (ie, ππ* or πσ*) of 24 does not change upon inclusion of dynamic electron correlation, the multi-configurational character of S2 and S3 decreases significantly as dynamic electron correlation is included (compare Tables 2 and 4).

In the case of the S1 state of 24 and 25, the effect of extensivity correction is similar and small, changing the ΔE values by at most 0.11 and 0.12 eV, for 25 and 24, respectively, both obtained with w4. For the S2 and S3 states of 24, the effect is significantly larger, decreasing the ΔE values of S2 and S3 by at most 0.32 and 0.22 eV, respectively (Table 4).

It is important to point out that, even considering only single internal → external excitations from the reference CSFs generated at the CAS (12,11) level (as in w1, see Table 1), for 24 the final number of CSFs is already very large, ~2.1 × 10^7 CSFs, because of the system size, number of active orbitals, and basis set. Therefore, if one includes single and double excitations, the calculation becomes computationally prohibitive, at least for an uncontracted multi-reference CI wavefunction, which is the type of MR-CI wavefunction used in this work. The same can be said even if one uses the same type of active space reduction based on the CASSCF occupation numbers, as has been done for the wavefunction w2 of 25.

One very important point is what type of wavefunction recovers a larger fraction of the electron correlation provided by a complete MR-CISD wavefunction, that is, an MR-CISD wavefunction based on a set of CAS(12,11) reference CSFs. As already mentioned, such type of calculation is not affordable, at least for an uncontracted wavefunction. However, one has two affordable options: (i) only single internal → external excitations, yielding an MR-CIS wavefunction (w1, see Table 1), or (ii) an MR-CISD wavefunction based on reference CSFs generated through limited excitations among the internal orbitals (from the occ to the antibonding orbitals described in Table 1), as in the case of w3 (for which only single occ→ anti-bonding excitations have been applied, see Table 1). Even though the answer concerning which type of wavefunction, w1 or w3, recovers a larger fraction of the electron correlation provided by a complete MR-CISD wavefunction could not be obtained, one can compare the effect due to the change from w1 to w3 on the properties here studied for 24 (Table 4). As case (ii) calculations based on higher than single excitations are not affordable, one cannot study the effect of the excitation level (within the internal orbitals given in Table 1) on the final properties. Instead, one can study the effect of removing the σ orbitals and, at the same time, increasing the excitation level within the active orbitals, through a comparison between w3 and w4 (Table 1).

As can be seen from Table 4, there are relatively large differences between the ΔE results obtained with w1 and with the MR-CISD wavefunctions (w3 and w4, see Table 1), varying from 0.31 to 1.15 eV, the maximum difference was obtained for S2 (2^{1}A') either with or without extensivity corrections. On the other hand, the differences between the ΔE values obtained with w3 and w4 for S1 (1^{1}A') and S2 (2^{1}A') are almost negligible (varying from 0.03 to 0.17 eV, see Table 4). For S3 the differences between the w3 and w4 results are much larger (with values of 0.63 and 0.64 eV, with and without extensivity corrections, respectively, see Table 4). Therefore, it is clear that the ΔE values obtained for S2 show by far the largest average variation among the wavefunctions (Table 4), which can be taken as an evidence of the greater difficulty in describing this state.

Similar to what has been obtained for 25, the effect due to the change from w1 to w1' is small, leading to changes of at most 0.09 and 0.06 eV in the ΔE values, with and without extensivity corrections, respectively. The f value of the S0 → S1 transition practically does not change, while those of the S0 → S2 and S0 → S3 transitions increase only by ~18% and ~20%, respectively (Table 4).

Based on the similarity between 24 and 25 and on the comparison between the results for 25 obtained from w2 and w4, it is expected that w4 is a good approximation to w2 also for 24, especially if extensivity correction is included, as aforementioned. Thus, w4 is not only the largest wavefunction used for 24 but can also be considered the most reliable one. Consequently, the discrepancies between w1/w1' and w4 are likely to be due to the unreliability of the former.

Despite the relatively large differences between the ΔE values (especially for S2, see Table 4), the nature of the states does not change with the wavefunction, even though there are some significant variations of the multi-configurational character of S2 and S3 (Table 4). Nevertheless, although the multi-configurational character of S2 is larger for w4, the weight of the ground-state configuration is virtually negligible in this case, different from what happens for w1, w1', and w3 (Table 4). For all three wavefunctions, there are significant contributions of the π3σ1* configuration in the ground-state wavefunction. For the S2 state, one has significant contributions of a double excitation (n1σ3σ3r2) only for w1 and w4 (Table 4), which is expected, as the reference CSFs of w3 do not include this double excitation (cf. Table 1).

For all three wavefunctions, the most intense transition of 24 remains the same (1^{1}A' → 2^{1}A'; S0 → S2, see Table 4). Based on the results obtained for the f values of 25 (and again based on the fact that 24 and 25 are similar), some decrease on the f values of 24 is to be expected (due to the change from w4 to w2) if w2 was not computationally prohibitive for 24. However, it is not expected that the most intense transition changes. Such transition for 24 (1^{1}A' → 2^{1}A') is approximately 11 times more intense than that of 25 (1^{1}A' → 1^{1}B2, compare the w4 results in Tables 3 and 4). This information, along with their corresponding excitation energies of 4.09 and 5.07 eV (obtained at the w4(+Q) level for 24 and 25, respectively, see Tables 3 and 4), can be helpful if one wants to discriminate these two isomers through UV-vis absorption spectroscopy.

By comparison between the CASPT2/aug-cc-pVTZ results for thiophenol, used as reference 23 (4.3, 4.5 and 5.1 eV for the S1, S2, and S3 states, respectively), and those obtained for 24, one can see how the ΔE values change in the thiophenol vs 24 pair. It is clear that the effect is by far the largest for S1 (as in the thiophenol vs 25 pair). Comparing the CASPT2 results with the results obtained including extensivity corrections (+Q), the excitation energies of S1 decrease by ~2.1 to 2.4 eV, depending on the wavefunction (Table 4). With exception of S2 at the w3(+Q) level
(where a slight increase of only 0.15 eV is obtained), the other \( \Delta E(+Q) \) values of S2 and S3 decrease from 0.41 to 0.96 eV, depending on the state and on the level of theory used, again compared to the CASPT2 results (Table 4).

The \( \Delta E(+Q) \) values of S1 (Table 4), along with the computed \( f \) values (although very small), are in line with the observation from ref. [2] that 24 is the only isomer that absorbs in the visible region. As discussed before, even though the first excited state of 25 is also in the visible region, its transition dipole moment vanishes by symmetry.

The experimental threshold for the photochemical transformations of 24 (\( \lambda < 427 \) nm = 2.90 eV) is consistent with excitation within the first band, associated with 1\(^1\)A\(^1\) (an n\(\pi^*\) state; see Table 4). While in thiophenol S1 is a \( \pi\pi^* \) state, in 24 it is an \( n\pi^* \) state, followed by a \( \pi\pi^* \) (S2) state and an \( n\pi^* \) (S3) state (Table 4). Thus, the nature of all three excited states changes as one goes from thiophenol\(^{[23]}\) to the thione isomer 24. For 24 and 25, the most intense band is due to a transition to a \( \pi\pi^* \) state, for all wavefunctions (Tables 3 and 4).

4 CONCLUSIONS

The first four singlet states of thiophenes 24 and 25 have been studied using several types of uncontracted MR-CI wavefunctions with the mixed aug-cc-PVDZ(C,H)/aug-cc-pVTZ(S) basis set. The excitation energies (\( \Delta E \)), oscillator strengths (\( f \)), and nature of the excited states have been investigated. The basis set effect has also been taken into account. It is the first time that the excited states of 24 and 25 are studied.

The largest MR-CI calculation was here performed for 25 because of its \( C_{2v} \) symmetry, achieving \(-3.6 \times 10^{18}\) CSFs. The change from thiophenol to 25 largely decreases the excitation energy of S1 (based on previous CASPT2/aug-cc-pVTZ\(^{[23]}\) and the \( \Delta E(+Q) \) results, see Table 3). In the case of S2, the effect is opposite but much smaller, increasing its excitation energy by at most 0.56 eV (at the w4(+Q) level, see Table 3). In the case of S2, the effect is almost negligible for the MR-CISD wavefunctions (w2 and w4, see Table 3).

Although S1 of 25 (1\(^1\)A\(^1\)) is in the visible region (with \( \Delta E(+Q) \) from \(-2.0\) to 2.4 eV, see Table 3), the 1\(^1\)A\(^1\) \( \rightarrow \) 1\(^1\)A\(^2\) transition is dipole-forbidden, by symmetry. The experimental threshold required for photochemical transformations of 25, \( \lambda < 332 \) nm (3.73 eV\(^{[2]}\)), is, according to our results, consistent with a transition within the first band. Therefore, some intensity gain is expected to be taking place around 3.73 eV, which is due to vibronic and/or spin-orbit coupling mechanisms. Intensity borrowing from the nearby band cannot be ruled out.

Only the nature of S3 (a \( \pi\pi^* \) state) is maintained as thiophenol changes to 25, with both S1 (also a \( \pi\pi^* \) state) and S2 (an \( n\sigma^* \) excited states changing their nature to \( n\pi^* \). On the other hand, for 24 the nature of the three first excited singlet states is \( n\pi^* \), \( \pi\pi^* \), and \( n\pi^* \), respectively. Thus, the nature of S1 to S3 changes upon the thiophenol \( \rightarrow \) 24 isomerization.

The \( \Delta E \) values decrease largely with the thiophenol \( \rightarrow \) 24 isomerization (again based on previous CASPT2/aug-cc-pVTZ\(^{[23]}\) and \( \Delta E(+Q) \) results), especially for S1. The only exception is observed for S2 with w3 (Table 4). The \( \Delta E(+Q) \) values, along with the computed \( f \) values (although very small), are in line with the observation from ref. [2] that 24 is the sole isomer absorbing in the visible region. The experimental threshold for the photochemical transformations of 24 (\( \lambda < 427 \) nm = 2.90 eV) is consistent with excitation within the first band, associated with the 1\(^1\)A\(^1\) (an \( n\pi^* \)) state.

Despite the relatively large differences obtained for the \( f \) values computed with different wavefunctions, the S0 \( \rightarrow \) S3 transition of 25 remains the most intense for all wavefunctions studied for this molecule. The same holds for the S0 \( \rightarrow \) S2 transition of 24.

Larger uncontracted MR-CI calculations still need to be performed (eg, MR-CISD based on a set of CAS(12,11) reference CSFs), when they become computationally feasible, to see how the aforementioned results are affected. Alternatively, the effect of using more accurate extensivity corrections, as multi-reference average quadratic, MR-AQCC, might be evaluated in relation to alterations in the excited states’ properties.

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