

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

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May 5, 2020

Abstract

Multi-reference configuration interaction, MR-CI (including extensivity corrections, named +Q) calculations have been performed on S_0 to S_3 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 have been employed, comprising MR-CI expansions as large as $\sim 374 \times 10^6$ configuration state functions. The nature of the studied excited states has been characterized. Vertical excitation energies (ΔE) and oscillator strengths (f) have been computed. The most intense transitions (S_0 - S_2 for **24** and S_0 - S_3 for **25**) do not change with the wavefunction, although a variation as large as ~ 1 eV has been obtained for the S_3 state of **24**. On the other hand, ΔE changes at most ~ 0.15 eV for **25**, as the wavefunction changes. The S_1 state of both thiones has $n\pi^*$ character and is in the visible region. For **24** S_2 and S_3 are $\pi\pi^*$ and $n\pi^*$ states, respectively, while for **25** the reverse order has been obtained. S_2 and S_3 are in the range from ~ 3.5 to 5.2 eV, at the highest level (MR-CI+Q). It is the first time that the excited states of the title molecules are studied. The computed results agree with the experimental onsets of photoreactions of thiones **24** and **25** found by Reva *et. al.* (*Phys. Chem. Chem. Phys.* **2015**, 17, 4888).

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