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Thiophenol: Photoinduced Hydrogen Migration

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Abstract: Reva *et al* [1] investigated some photoinduced H-transfer isomerization reactions of thiophenol in a solid argon matrix (Figure 1). In this study,

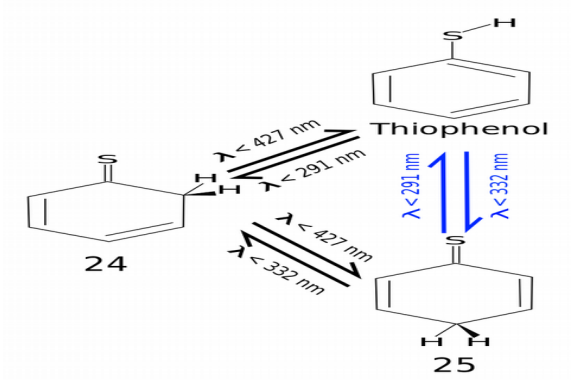

Figure 1: Photoinduced reactions of thiophenol studied in a solid argon matrix [1]. The reactions in blue were not confirmed or discarded in this experiment.

the photogenerated isomers – cyclohexa-2,4-diene-1-thione (**24**) and cyclohexa-2,5-diene-1-thione (**25**) – have never been observed so far. In order to explain the experimental results, our group has performed high level excited-state calculations (CASSCF and MR-CI) to study the reactions thiophenol→**24,** **24**→**25** and thiofenol→**25**. This is the first theoretical study concerning the photochemistry reactions studied by Reva *et al* [1] . The active space CAS consists of twelve electrons distributed among eleven orbitals (Figure 2). Vertical excitation energies of thiophenol

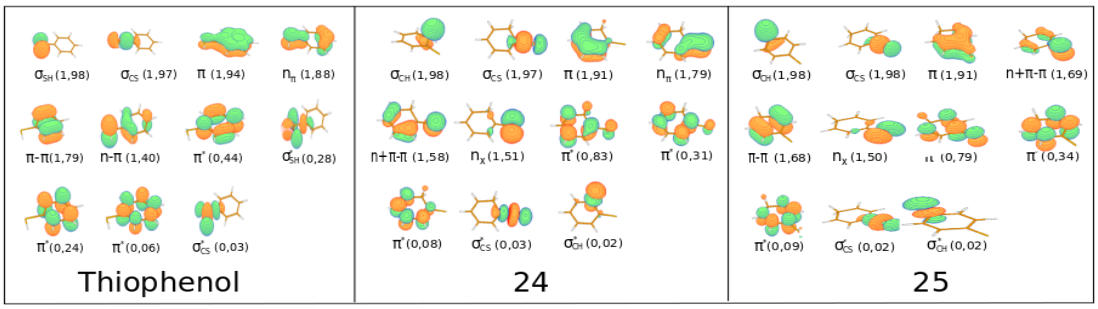

Figure 2: MO diagrams and associated occupation numbers for three lowest excited states of thiophenol, and thiones 24 and 25 at the CAS(12,11) level.

calculated at CASSCF and MR-CISD levels have been compared with the CASPT2 results [2]. The reaction paths were generated by linear interpolation, and the obtained geometries were used to compute the vertical excitation energies at the CASSCF level. So far all calculations were performed with aug-cc-pVDZ basis. The potential energy profiles of thiophenol→**24** and **24**→**25** are displayed in Figure 3:

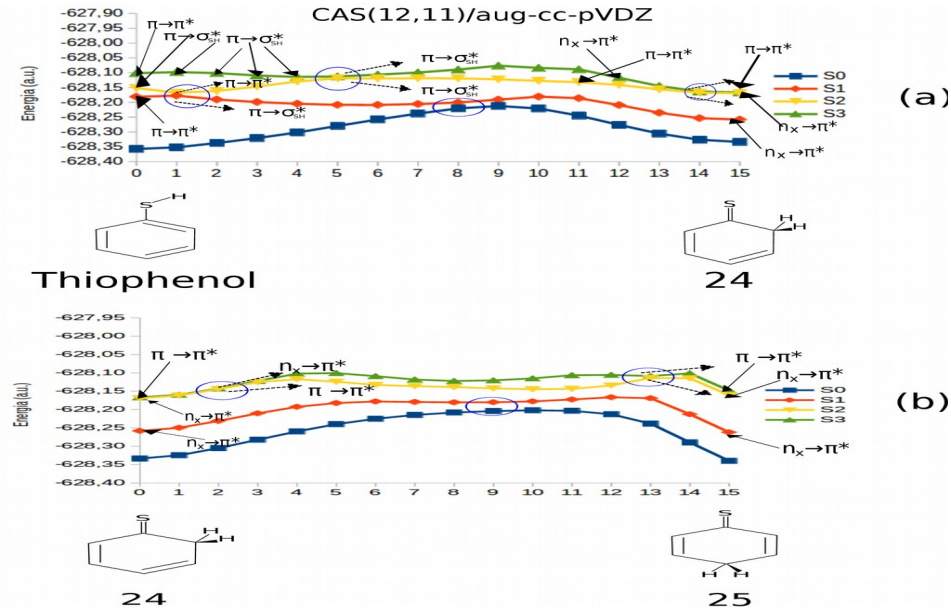

Figure 3: Potential energy profiles of the reactions (a) thiophenol→24 and (b) 24→25 at CAS(12,11) level using the aug-cc-pVDZ basis.

As it can be seen from Figure 3, several conical intersections (blues circles) are likely to take place. In (a) their occurrence are consistent with formation of **24** from all three studied excited states. The same holds for the reaction **24**→**25** (b), although in this case more vibrational energy may be required. The conical intersections between S_0 and S_1 in (a) and (b) suggests either formation of the product or regeneration of the reactants, from the photoreaction starting in S_1. Preliminary results suggest that the reaction thiophenol→**25** actually involves **24** as an intermediate. COLUMBUS program system has been used for most of the calculations.

Key-words: thiophenol, photoinduced H migration, CASSCF, MR-CISD, conical intersection.
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References:
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[2] M. N. R. Ashfold, G. A. King, D. Murdock, M. G. D. Nix, T. A. A. Oliver, A. G. Sage, Physical Chemistry Chemical Physics, 12, 1218, (2010).