# Tautomerism and thermodynamic stability of two mercapto-1,3,4-thiadiazoles

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1,3,4-thiadiazoles are five-membered heterocycles containing one sulphur and two nitrogen atoms in the positions 1, 3 and 4 of the ring. The substitutions into the 2' or 5' position of the ring result in highly activated species that readily react to yield diverse derivatives [1]. In addition, the existence of thiol and thione tautomeric forms is one of the most interesting properties of mercapto-thiadiazoles, influencing their reactivity. Due to these characteristics, 1,3,4-thiadiazole derivatives are widely applied in pharmaceutical, agricultural, and materials chemistry [1,2].

This work presents an experimental and computational thermochemical study of 2-mercapto-1,3,4-thiadiazole and 2-mercapto-5-methyl-1,3,4-thiadiazole. The experimental data were determined from combustion calorimetry and from Knudsen effusion experiments, being used to derive the respective gas-phase standard molar enthalpy of formation. The thermodynamic stability of the compounds is analyzed based on their corresponding gas-phase standard molar Gibbs energies of formation.

Additional quantum chemical calculations were carried out for both isolated molecules. Also, the tautomeric equilibrium of both compounds, presented in figure 1, is evaluated and the inherent activation energy in gaseous phase is also calculated, as well as, in aqueous solution and DMSO.

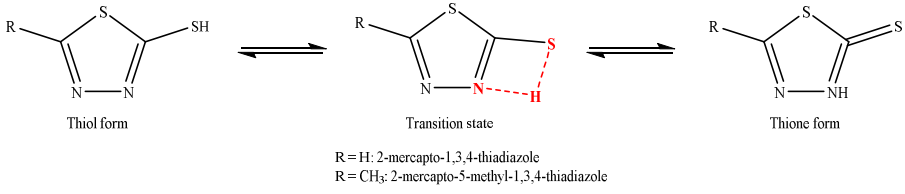


**Figure 1.** Thiol/thione tautomeric forms of 2-mercapto- and 2-mercapto-5-methyl-1,3,4-thiadiazole.

*Acknowledgements:* This work was developed under the funding of the project UIDB/00081/2020, awarded to CIQUP, financed by FCT, Lisbon, Portugal. Ana L.R. Silva thanks FCT/MCTES for her contract under Stimulus of Scientific Employment 2017 (CEECIND/01161/2017).

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