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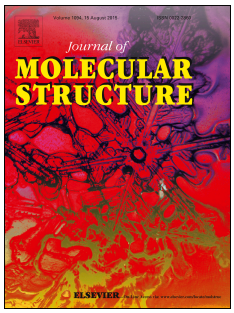

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Tautomerism in 4-chlorophenyl benzoylcarbamodithioate: Experimental and DFT study

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Abstract

The title dithiocarbamate compound was synthesised, and characterised by means of spectroscopic and single-crystal X-ray diffraction methods. Density functional theory method with the 6−311++G(d,p) basis set was employed to affirm the spectroscopic and structural properties and also to study the tautomerism in the compound. The obtained theoretical parameters clearly support the experimental findings. Among the six structural forms of the title compound, the *syn*-keto-amine-thione is found to be the most stable one, and the stability sequence is as the followings: *syn*-keto-amine-thione > *anti*-enol-imine-thione > *anti*-keto-amine-thione > *anti*-keto-imine-thiol > *syn*-keto-imine-thiol > *syn*-enol-imine-thione. The energy difference between the *anti* and *syn* forms changes from ca. 8 to 59 kJ mol^{-1} with or without barriers. The energetic and thermodynamic findings of the *syn*-keto-amine-thione ⇄ *syn*-keto-imine-thiol reaction display that the single proton exchange is unfavoured in both directions. Although the reverse barrier energy of the *anti*-enol-imine-thione ⇄ *anti*-keto-imine-thiol tautomeric transformation is found to be small, neither the forward nor the reverse reaction appears to happen from the thermodynamic point of view.

Keywords: crystal structure; spectroscopy; density functional theory; rotamerism; tautomerism