



Title

**Conversion of thiol to homodisulfide-Schiff base derivative:
Synthesis, molecular structure, crystal structure and DFT studies**

Abstract

Oxidative coupling of thiols to the corresponding disulfides under neutral and mild conditions is an important pathway in synthetic chemistry and biological processes. Facile conversion of a thiol-Schiff base (obtained from the condensation of 2-hydroxynaphthaldehyde and 2-aminothiophenol) to the corresponding homodisulfide derivative is described. The molecular structure and stoichiometry of the thiol (1) and disulfide (2) compounds were characterized by analytical and spectroscopic techniques. The structure of the disulfide derivative was also confirmed by single crystal X-ray analysis. Theoretical calculations based on density functional theory (DFT) were established to verify the structures of the thiol in both solid and solution forms as well as the structure of the disulfide. The optimized geometrical parameters, natural charges on active centers, and energy of the ground state for the thiol and homodisulfide derivatives were computed and analyzed by using basis set 6-31G (d,p). The global chemical reactivity descriptors were estimated from the energy of the HOMO and LUMO orbitals. The infrared spectrum of 1 exhibited a sharp band at 3262 cm^{-1} . This band was assigned to the stretching frequency of the HN^+ group, where a proton transferred from the SH group to the nitrogen of azomethine. Also, the IR spectrum did not exhibit a band due to the OH group. This could be due to the presence of intramolecular hydrogen bonding between the OH and S-moieties. The ^1H NMR spectrum of 1 in DMSO- d_6 displayed two singlets at 10.54 and 8.44 ppm due to OH and $\text{CH}=\text{N}$ protons, respectively. Interestingly, the ^1H NMR spectrum of 1 displayed minor signals at 15.00 and 9.75 ppm due to the presence of traces of disulfide dimer. The IR spectrum of the homodisulfide derivative (2) displayed a broad band at 3442 cm^{-1} due to free OH groups, the spectrum did not show bands due to the HN^+ group as was shown in the thiol spectrum. This is another evidence that the formation of the HN^+ group in the thiol derivative was performed by the transfer of the SH proton to the azomethine nitrogen. The S-S bond stretching frequency usually occurred in the range $500\text{-}540\text{ cm}^{-1}$. The ^1H NMR spectrum of 2 displayed a sharp signal at 15.00 ppm due to the OH protons. The sharpness and lower field position indicated that these OH groups are not involved in intramolecular hydrogen bonding. The crystal structure of the disulfide compound showed that the compound is symmetrical with a C_2 axis of symmetry passing through the S-S bond. The crystal analysis proved that the compound crystallized in triclinic crystal symmetry with space group P1 and a Z value of 4. Adopting this mild condition in preparing such compounds has a significant effect on preparing organic compounds and pharmaceuticals.