

A Theoretical Study of the Tautomerism and Vibrational Spectra of 4,5-Diamine-2,6-dimercaptopyrimidine

R. A. Timm,^a J. A. Bonacin,^a A. L. B. Formiga^b and H. E. Toma^{*a}

^aInstituto de Química, Universidade de São Paulo, CP 26077, 05513-970 São Paulo-SP, Brazil

^bInstituto de Química, Universidade Estadual do Rio de Janeiro, Rio de Janeiro-RJ, Brazil

A 4,5-diamina-2,6-dimercaptopyrimidina (DADMCP) constitui uma molécula multifuncional que apresenta uma tautomeria bastante complexa, com nove formas isoméricas possíveis. O estudo da tautomeria nesse composto foi realizado por meio da espectroscopia FTIR em associação com cálculos *ab-initio* HF/SCF e DFT. De acordo com os resultados teóricos, três tautômeros são favorecidos energeticamente, sendo a tiona a forma a mais estável. Os espectros vibracionais das formas tautoméricas mais estáveis foram simulados através de cálculos de DFT, permitindo a atribuição e elucidação do quadro complexo de bandas vibracionais observado experimentalmente, envolvendo a mistura de isômeros.

The 4,5-diamine-2,6-dimercaptopyrimidine (DADMCP) compound is an interesting multifunctional species exhibiting a rather complex tautomerism, encompassing nine tautomeric forms. Investigation of tautomerism in this compound has been carried out by means of FTIR spectroscopy, in association with *ab-initio* HF/SCF and DFT calculations. According to this study three tautomers are energetically favored; the thione form being the most stable one. The theoretical vibrational spectra of such tautomeric forms have been successfully simulated by means of DFT calculations, allowing the elucidation and assignment of the complex composition of the vibrational bands observed for the mixture of isomers.

Keywords: mercaptopyrimidines, DFT calculations, tautomerism, spectral simulation

Introduction

Mercaptopyrimidines are interesting compounds, which have been widely studied over the past few years¹ because of their many interesting applications, especially in coordination chemistry. By incorporating both S and N atoms in their structures, they are able to bind transition metal ions, acting as monodentate² and more frequently as chelating and bridging ligands.³⁻⁵ These compounds exhibit tautomeric equilibrium between the thiol (>C-SH) and thione (>C=S) forms, as a consequence of the highly mobile protons in their structure.⁶⁻⁸ In fact, thione-thiol tautomeric equilibrium have attracted great experimental⁹⁻¹³ and theoretical interest¹⁴⁻¹⁷ in chemistry and biochemistry. These forms can mutually interchange *via* intramolecular proton transfer between the nitrogen and the nearby carbonyl sulfur. The interchange mechanism is solvent dependent; usually, the thione form predominates in polar

solvent while the thiol is favorable in gas phase or nonpolar solvents.^{14,16,18,19}

In this article, we present a theoretical study on the tautomerism of 4,5-diamine-2,6-dimercaptopyrimidine (DADMCP). This compound is an interesting multifunctional species capable of undergoing electrochemical polymerization and of sequestering transition metal ions.²⁰ Experimental support for the existence of the tautomeric forms of this molecule was obtained from FTIR spectroscopy, in analogy with a recent work on violuric acid and 6-amino-5-nitrouracil.²¹ Further insight into the molecular structures was provided by theoretical calculations using *ab-initio* Hartree-Fock Self-Consistent Field (HF/SCF) and the density functional theory (DFT) approaches.

Experimental

The compound 4,5-diamine-2,6-dimercaptopyrimidine was obtained from Aldrich. FTIR spectra of the solid

*e-mail: henetoma@iq.usp.br

samples in the range of 4,000-400 cm^{-1} were recorded on a Shimadzu FTIR-8300 spectrophotometer, using KBr pellets. The NIR spectra in the range of 29,000-4,000 cm^{-1} were recorded on a FieldSpec fiber optics instrument from Analytical Spectral Devices (ASD).

Computational calculations were carried out using the GAMESS(R4) software²² for geometry optimization. In all cases, a convergence criterion of 10^{-4} kcal \AA^{-1} mol $^{-1}$ was used in a conjugate gradient algorithm. Molecular orbitals were expanded using the atomic 6-31G(d,p) basis set to solve the Hartree-Fock (HF) equations as well as the Kohn-Sham ones (DFT). The gradient-corrected density functional methodology employed in DFT calculation was the B3LYP hybrid.²³⁻²⁵ The harmonic vibrational frequencies and intensities were calculated at the same levels of theory with the analytical evaluation of second derivatives of energy as a function of atomic coordinates and the calculated intensities were utilized to generate the theoretical spectra. Low and high frequencies were scaled by factors of 1.01 and 1.06, respectively, and zero-point energies by a factor of 0.9806, as recommended by Scott and Radom.²⁶

The theoretical vibrational spectra shown in Figure 3, were calculated from the sum of Gaussian shaped bands, based on the equation:²⁴

$$T(\omega) = 2,174 \times 10^8 \sum_I \frac{f_I}{\Delta_{1/2}} \exp\left(-2,773 \frac{(\omega - \omega_I)^2}{\Delta_{1/2}^2}\right)$$

where T is transmittance, and assuming half-bandwidths ($\Delta_{1/2}$) of 40 cm^{-1} . The sum in the equation includes all allowed vibration transitions with energies, ω_I (expressed in cm^{-1}), and oscillator strengths, f_I which were obtained from the theoretical calculations. The total integrated intensity is equal to the sum of the oscillator strengths:

$$4,319 \times 10^{-9} \int \varepsilon(\omega) d\omega = \sum_I f_I$$

Results and Discussion

Theoretical investigation of DADMCP compound showed nine possible tautomers, here denoted 1 to 9 (Figure 1). The geometry of each one was optimized by *ab-initio* RHF/SCF and DFT methods. More than one conformer was found for each tautomer, and the most stable conformer was chosen for further analysis. The energies of each tautomer are shown in Table 1. The usefulness of DFT methods to deal with the tautomerism of nucleic acid bases is a rather well established point. In particular, vibrational frequencies and zero-point energies have been estimated

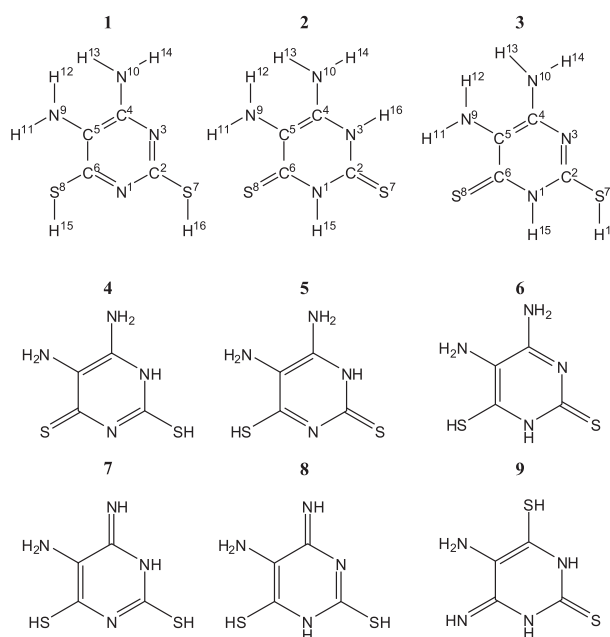


Figure 1. Tautomeric forms of 4,5-diamine-2,6-dimercapto-pyrimidine.

very accurately, and frequently with errors smaller than those reported using MP2 theory²⁷⁻²⁹. According to HF/SCF and DFT calculations, the order of stability is **2** > **3** > **1** > **6** > **9** > **5** > **4** > **7** > **8**. The dithione form is expected to be the most stable one (tautomer **2**).

Based on these results, the vibrational spectra of the three most stable tautomers of DADMCP (**1**, **2** and **3**) were calculated theoretically, as shown in Figure 3. In fact, the DFT frequencies provided a good insight into the vibrational structure of the three tautomeric species, as shown in Tables 2-4.

Table 1. HF/SCF, DFT and Zero-point theoretical energies (kcal mol $^{-1}$) for the 4,5-diamine-2,6-dimercapto-pyrimidine tautomers (vacuum) and energy difference with respect to tautomer **2**

| Tautomer | HF/SCF | ΔE | DFT | ΔE | ZPE | ΔE^{ZPE} |
|----------|------------|------------|------------|------------|------|-------------------------|
| 1 | -732,895.2 | 5.8 | -734,976.5 | 9.7 | 66.6 | 4.6 |
| 2 | -732,901.0 | 0 | -734,986.2 | 0 | 71.7 | 0 |
| 3 | -732,896.4 | 4.5 | -734,980.3 | 5.9 | 69.3 | 3.5 |
| 4 | -732,875.2 | 25.8 | -734,960.8 | 25.4 | | |
| 5 | -732,882.2 | 18.7 | -734,967.8 | 18.4 | | |
| 6 | -732,886.5 | 14.5 | -734,970.4 | 15.8 | | |
| 7 | -732,871.4 | 29.6 | -734,954.7 | 31.5 | | |
| 8 | -732,864.5 | 36.4 | -734,950.1 | 36.1 | | |
| 9 | -732,884.7 | 16.2 | -734,969.8 | 16.4 | | |

Zero-point vibrational energies for the three tautomers confirmed the stability order, but the energy gap is large enough to indicate tautomer **2** should predominate in gas phase. However, for this tautomer, the comparison of the theoretical and the experimental FTIR spectrum of the

DADMCP species (Figure 3) shows that the number of bands in the experimental spectrum is higher than for the predicted one, specially in the 400-1700 cm^{-1} region. For this reason, the occurrence of a mixture of tautomers seems indeed rather plausible in the solid state.

The experimental infrared spectrum of DADMCP is shown in Figure 2, revealing a rather complex composition of the vibration bands for this compound. In a first approximation, the group of broad bands from 3600 to 2800 cm^{-1} can be attributed to $\nu_{\text{as}}(\text{N-H})$ and $\nu_{\text{s}}(\text{N-H})$ of the free and hydrogen bonded molecules in the solid. The shoulders around 2600 cm^{-1} can be tentatively ascribed to $\nu(\text{S-H})$. The bands at 1565 and 1647 cm^{-1} can be attributed to $\delta(\text{N-H})$ in NH_2 groups. The bands at 1300 and 1346 cm^{-1} can be assigned to $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ vibrations. The remaining bands are associated with amine groups and aromatic ring vibrations.

A correlation study, trying to match each pair of experimental and theoretical vibrational band, has been carried out, as shown in Tables 2-4. Tautomer 1 exhibits a

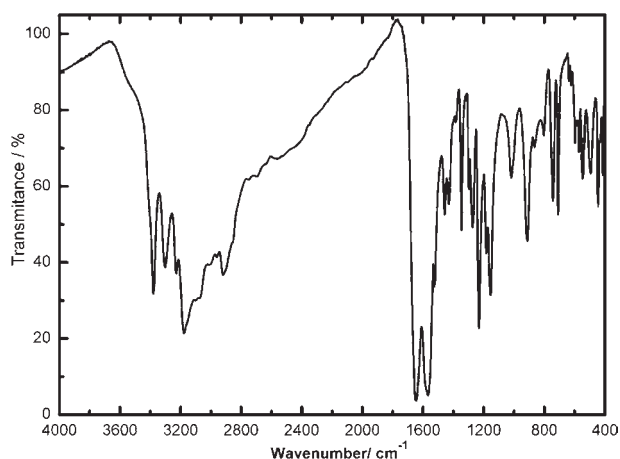


Figure 2. FTIR spectrum of the 4,5-diamine-2,6-dimercaptopyrimidine compound (KBr pellets).

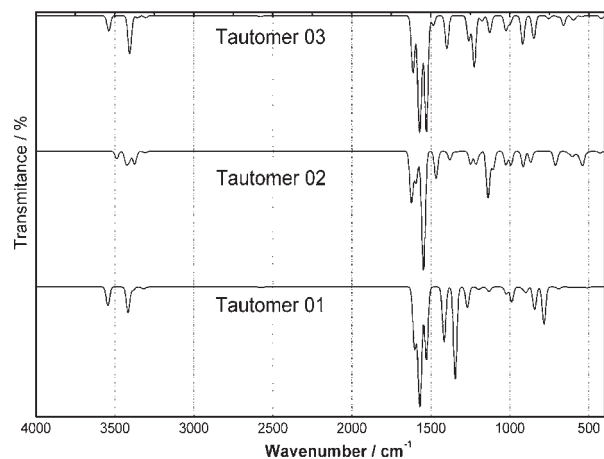


Figure 3. Theoretical FTIR spectra of the DADMCP tautomers 1, 2 and 3.

Table 2. Experimental and theoretical vibrational spectrum* of tautomer 1

| Mode | Exp. / cm^{-1} | Theor. / cm^{-1} | Assignments |
|------|-------------------------|---------------------------|--|
| 42 | 3565 | 3521 | $\nu_{\text{as}}\text{N}_{10}\text{H}_{13,14}$ [98.5] |
| 41 | 3379 | 3387 | $\nu_{\text{s}}\text{N}_{10}\text{H}_{13,14}$ [98.8] |
| 40 | 3300 | 3319 | $\nu_{\text{as}}\text{N}_9\text{H}_{11,12}$ [99.4] |
| 39 | 3230 | 3261 | $\nu_{\text{s}}\text{N}_9\text{H}_{11,12}$ [99.1] |
| 38 | 2693 | 2678 | $\nu\text{S}_8\text{H}_{15}$ [97.3] |
| 37 | 2577 | 2662 | $\nu\text{S}_7\text{H}_{16}$ [97.3] |
| 36 | 1647 | 1648 | $\delta\text{N}_{10}\text{H}_{13,14}$ [44.0] + $\delta\text{N}_9\text{H}_{11,12}$ [42.1] + $\nu\text{N}_3\text{C}_{4,5}$ [9.5] |
| 35 | 1565 | 1626 | $\delta\text{N}_9\text{H}_{11,12}$ [57.1] + $\delta\text{N}_{10}\text{H}_{13,14}$ [36.4] |
| 34 | 1525 | 1577 | $(\nu\text{C}_{4,5,6} + \delta\text{C}_4\text{N}_{10}\text{H}_{13} + \nu(\text{C}_5\text{-N}_9\text{H}_{11,12}))$ [70.3] + $\nu\text{N}_3\text{C}_{4,5}$ [16.7] + $\delta\text{S}_8\text{H}_{15}$ [8.3] |
| 33 | 1462 | 1541 | $\delta\text{N}_{10}\text{H}_{13,14}$ [30.3] + $\delta\text{N}_9\text{H}_{11,12}$ [28.6] + $\nu\text{C}_{4,5,6}$ [19.3] + $\nu\text{N}_3\text{C}_4\text{N}_1$ [16.5] + $\delta\text{S}_7\text{H}_{16}$ [3.5] |
| 32 | 1430 | 1471 | $(\nu\text{C}_4\text{N}_{10} + \delta\text{N}_{10}\text{H}_{13,14})$ [61.3] + $(\nu\text{C}_{5,6} + \nu(\text{C}_5\text{-N}_9\text{H}_{11,12}))$ [18.7] + $\nu\text{N}_3\text{C}_2\text{N}_1$ [12.1] |
| 31 | 1346 | 1370 | $(\nu\text{C}_{4,5,6} + \nu(\text{C}_5\text{-N}_9\text{H}_{11,12}))$ [45.4] + $\nu\text{N}_3\text{C}_2\text{N}_1$ [34.2] + $\delta\text{N}_{10}\text{H}_{13,14}$ [14.6] |
| 30 | 1300 | 1294 | $(\nu\text{C}_6\text{N}_1\text{C}_2 + \nu\text{C}_2\text{S}_7)$ [45.8] + $\nu\text{N}_3\text{C}_{4,5}$ [21.3] + $\delta\text{N}_{10}\text{H}_{13,14}$ [16.2] + $\delta\text{N}_9\text{H}_{11,12}$ [12.2] |
| 29 | 1276 | 1270 | $\rho\text{N}_{10}\text{H}_{13,14}$ [40.9] + $\nu\text{C}_6\text{N}_1\text{C}_2$ [22.9] + $\nu\text{N}_3\text{C}_{4,5}$ [17.5] + $\delta\text{N}_9\text{H}_{11,12}$ [8.4] + $\delta\text{S}_8\text{H}_{15}$ [8.1] |
| 28 | 1232 | 1218 | $\nu(\text{C}_5\text{-N}_9\text{H}_{11,12})$ [31.7] + $\rho\text{N}_{10}\text{H}_{13,14}$ [31.1] + $\nu\text{C}_6\text{N}_1\text{C}_2$ [19.7] + $\delta\text{S}_8\text{H}_{15}$ [8.8] + $\nu\text{N}_3\text{C}_6$ [5.8] |
| 27 | 1182 | 1153 | $\nu\text{N}_9\text{H}_{11,12}$ [92.4] |
| 26 | 1152 | 1084 | $\rho\text{N}_{10}\text{H}_{13,14}$ [55] + $\nu\text{N}_3\text{C}_4\text{N}_{10}$ [13.8] + $\delta\text{S}_8\text{H}_{15}$ [10.1] + $\delta\text{S}_7\text{H}_{16}$ [5.8] + $\nu\text{C}_{4,5,6}$ [9.2] |
| 25 | 1015 | 1028 | $\delta\text{S}_8\text{H}_{15}$ [43.9] + $(\nu\text{C}_{4,5,6} + \nu\text{C}_4\text{-N}_{10}\text{H}_{13,14})$ [28.8] + $\nu\text{N}_3\text{C}_2\text{N}_1$ [15.3] + $\delta\text{N}_9\text{H}_{11,12}$ [8.9] |
| 24 | | 981 | $\delta\text{S}_7\text{H}_{16}$ [45.3] + $\rho\text{N}_{10}\text{H}_{13,14}$ [17.0] + $\nu\text{C}_6\text{N}_1\text{C}_2$ [13.9] + $\delta\text{S}_7\text{H}_{16}$ [12.6] + $\nu\text{N}_3\text{C}_{4,5}$ [7.9] |
| 23 | 910 | 917 | $\delta\text{S}_7\text{H}_{16}$ [59.5] + $\delta\text{S}_8\text{H}_{15}$ [11.9] + $\nu\text{C}_6\text{N}_1\text{C}_2$ [10.7] + $\rho\text{N}_{10}\text{H}_{13,14}$ [9.6] + $\nu\text{N}_3\text{C}_{4,5}$ [4.5] |
| 22 | 863 | 863 | $\omega\text{N}_9\text{H}_{11,12}$ [27.0] + $(\delta\text{S}_7\text{H}_{16} + \nu\text{C}_2\text{S}_7)$ [20.2] + $(\delta\text{S}_8\text{H}_{15} + \nu\text{C}_6\text{S}_8)$ [21.0] + $\nu\text{N}_3\text{C}_{4,5}$ [16.4] + $\rho\text{N}_{10}\text{H}_{13,14}$ [9.9] |
| 21 | 806 | 790 | $\omega\text{N}_9\text{H}_{11,12}$ [72.8] + $\rho\text{N}_{10}\text{H}_{13,14}$ [9.5] + $\nu\text{N}_3\text{C}_{4,5}$ [8.2] + $\delta\text{S}_7\text{H}_{16}$ [3.0] |
| 20 | 746 | 782 | τring [56.6] + $\tau\text{N}_9\text{H}_{11,12}$ [34.5] |
| 19 | 712 | 718 | $\omega\text{N}_9\text{H}_{11,12}$ [32.4] + ring breath [35.4] + $\rho\text{N}_{10}\text{H}_{13,14}$ [20.9] + $\delta\text{S}_8\text{H}_{15}$ [11.1] |
| 18 | 639 | 681 | τring [52.3] + $\tau\text{N}_{10}\text{H}_{13,14}$ [30.5] + $\tau\text{N}_9\text{H}_{11,12}$ [17.1] |
| 17 | 621 | 629 | $\tau\text{N}_{10}\text{H}_{13,14}$ [75.4] + $\rho\text{N}_9\text{H}_{11,12}$ [12.4] + τring [10.2] |
| 16 | 600 | 608 | τring [60.7] + $\rho\text{N}_9\text{H}_{11,12}$ [27.1] |
| 15 | 571 | 577 | Ring breath [38.6] + $\rho\text{N}_{10}\text{H}_{13,14}$ [27.7] + $\omega\text{N}_9\text{H}_{11,12}$ [19.4] + $(\delta\text{S}_8\text{H}_{15} + \delta\text{S}_7\text{H}_{16})$ [14.7] |
| 14 | 545 | 545 | $\rho\text{N}_{10}\text{H}_{13,14}$ [31.3] + δring [28.9] + $\omega\text{N}_9\text{H}_{11,12}$ [21.1] + $(\delta\text{S}_8\text{H}_{15} + \delta\text{S}_7\text{H}_{16})$ [18.6] |
| 13 | 446 | 408 | δ ring |
| 12 | 412 | 395 | ring breath |

*Fractional composition of the vibrational modes are shown in parenthesis.

Table 3. Experimental and theoretical vibrational spectrum of tautomer 2*

| Mode | Exp. / cm ⁻¹ | Theor. / cm ⁻¹ | Assignments |
|------|-------------------------|---------------------------|--|
| 42 | 3595 | 3436 | $\nu_{as} N_{10} H_{13,14}$ [98.4] |
| 41 | 3379 | 3394 | $\nu N_3 H_{16}$ [95.3] |
| 40 | 3300 | 3340 | $\nu N_1 H_{15}$ [95.0] |
| 39 | 3230 | 3294 | $\nu_{as} N_9 H_{11,12}$ [65.0] + $\nu_{as} N_{10} H_{13,14}$ [34.3] |
| 38 | 3177 | 3291 | $\nu_{as} N_{10} H_{13,14}$ [58.7] + $\nu_{as} N_9 H_{11,12}$ [39.9] |
| 37 | | 3235 | $\nu N_9 H_{11,12}$ [98.0] |
| 36 | 1647 | 1676 | $\pi N_9 H_{11,12}$ [58.7] + $\delta N_{10} H_{13,14}$ [19.2] + $\nu C_{4,5}$ [10.5] + $\delta C_2 N_3 H_{16}$ [8.7] |
| 35 | | 1632 | $\pi N_9 H_{11,12}$ [49.2] + $\delta N_{10} H_{13,14}$ [37.3] + $\delta C_2 N_3 H_{16}$ [6.9] + $\nu C_{4,5}$ [5.5] |
| 34 | 1565 | 1586 | $\delta N_{10} H_{13,14}$ [42.9] + $\pi N_9 H_{11,12}$ [22.5] + $\delta C_2 N_3 H_{16}$ [20.1] + $\nu C_{4,5}$ [10.4] |
| 33 | | 1574 | $(\delta N_3 H_{16} + \delta N_1 H_{15})$ [56.7] + $\pi N_9 H_{11,12}$ [13.7] + $\delta N_{10} H_{13,14}$ [11.5] + $\nu C_{4,5}$ [10.1] + $(\nu C_2 S_7 + \nu C_6 S_8)$ [8.0] |
| 32 | 1462 | 1500 | $(\nu C_2 N_1 + \delta N_1 H_{15})$ [36.8] + $(\nu C_4 N_3 + \delta N_3 H_{16})$ [23.0] + $\nu C_{5,6}$ [14.8] + $\delta N_{10} H_{13,14}$ [15.4] + $\pi N_9 H_{11,12}$ [8.5] |
| 31 | 1430 | 1400 | $\nu(C_4-N_{10} H_{13,14})$ [38.6] + $\nu C_{5,6}$ [25.7] + $\nu C_2 N_3$ [20.8] + $\delta N_1 H_{15}$ [14.8] |
| 30 | 1386 | 1386 | $(\delta N_1 H_{15} + \delta N_3 H_{16})$ [57.1] + $\nu(C_4-N_{10} H_{13,14})$ [22.4] + $(\nu C_6 S_8 + \nu C_2 S_7)$ [11.8] + $\nu(C_5-N_9 H_{11,12})$ [8.5] |
| 29 | 1300 | 1292 | $(\nu N_1 C_2 N_3 + \delta N_3 H_{16})$ [36.1] + $\pi N_9 H_{11,12}$ [28.4] + $\rho N_{10} H_{13,14}$ [17.8] + $\nu C_{4,5,6}$ [17.5] |
| 28 | 1276 | 1276 | $\nu C_5 N_9 H_{11,12}$ [33.8] + $\rho N_{10} H_{13,14}$ [28.1] + $(\nu_{as} C_2 N_3 C_4 + \delta N_3 H_{16})$ [28.1] + $\nu C_6 N_1$ [9.8] |
| 27 | 1232 | 1237 | $\tau N_9 H_{11,12}$ [76.6] + $(\nu N_1 C_2 N_3 + \delta N_3 H_{16})$ [16.0] + $\pi C_{4,5,6}$ [7.2] |
| 26 | 1182 | 1166 | $(\nu N_1 C_6 + \delta N_1 H_{15})$ [40.5] + $\rho N_{10} H_{13,14}$ [22.6] + $(\nu N_3 C_2 + \delta N_3 H_{16})$ [17.9] + $\nu N_9 C_5$ [17.8] |
| 25 | 1156 | 1142 | $(\rho N_{10} H_{13,14} + C_4 N_{10})$ [31.2] + $(\nu C_2 N_1 C_6 + \delta N_1 H_{15})$ [25.6] + $\delta N_3 H_{16}$ [25.7] + $\omega N_9 H_{11,12}$ [13.8] |
| 24 | | 1062 | $\rho N_{10} H_{13,14}$ [50.1] + $(\delta N_{13} H_{16} + \delta N_1 H_{15})$ [22.7] + $(\nu C_2 S_7 + \nu C_6 S_8)$ [13.7] + $\omega N_9 H_{11,12}$ [8.2] + $\nu C_{4,5}$ [5.6] |
| 23 | 1015 | 1025 | $\nu_{as} C_2 N_3 C_4$ [29.2] + $\nu C_{4,5} N_1$ [24.7] + $\omega N_9 H_{11,12}$ [24.5] + $\rho N_{10} H_{13,14}$ [21.6] |
| 22 | 910 | 942 | $\omega N_9 H_{11,12}$ [50.7] + $\nu N_1 C_2 N_3$ [23.7] + $\rho N_{10} H_{13,14}$ [17.7] + $\nu C_{4,5,6}$ [7.7] |
| 21 | 863 | 902 | $\omega N_9 H_{11,12}$ [52.0] + $\nu C_6 S_8$ [21.4] + $\delta C_2 N_3 C_2$ [18.8] + $\rho N_{10} H_{13,14}$ [7.7] |
| 20 | 746 | 745 | $(\delta C_{4,5,6} + \nu C_5 N_9)$ [38.1] + $\delta N_1 C_2 N_3$ [40.2] + $\rho N_{10} H_{13,14}$ [21.5] |
| 19 | 712 | 727 | $\pi N_1 H_{15}$ [65.4] + $\pi C_{4,5,6}$ [23.6] + $\tau N_3 H_{16}$ [9.3] |
| 18 | 640 | 707 | $\pi N_1 C_2 N_3$ [28.9] + $\tau N_{10} H_{13,14}$ [26.2] + $\pi C_{4,5,6}$ [23.6] + $\omega N_9 H_{11,12}$ [21.1] |
| 17 | 623 | 645 | $\tau N_{10} H_{13,14}$ [51.8] + $\pi C_6 N_1 C_5$ [23.3] + $\omega N_9 H_{11,12}$ [16.1] + $\pi C_4 N_3 C_2$ [8.8] |
| 16 | 600 | 618 | $\pi N_1 C_2 N_3$ [45.3] + $\tau N_{10} H_{13,14}$ [24.9] + $\omega N_9 H_{11,12}$ [15.1] + $\pi C_{4,5,6}$ [14.6] |
| 15 | 584 | 591 | $\pi N_3 H_{16}$ [33.4] + $\tau N_{10} H_{13,14}$ [24.2] + $\tau C_{4,5,6}$ [18.7] + $\tau N_1 H_{15}$ [11.1] + $\tau N_9 H_{11,12}$ [7.5] |
| 14 | 571 | 570 | $\delta ring$ [85.0] + $\pi N_3 H_{16}$ [15.0] |
| 13 | 545 | 563 | $\pi N_3 H_{16}$ [32.6] + $\omega N_{10} H_{13,14}$ [29.4] + $(\pi C_6 S_8 + \pi C_2 S_7)$ [11.1] + $\omega N_9 H_{11,12}$ [10.7] + $\pi N_1 H_{15}$ [9.4] |
| 12 | 495 | 524 | $\delta ring$ [81.9] + $\pi N_3 H_{16}$ [18.1] |

*Fractional composition of the vibrational modes are shown in parenthesis

Table 4. Experimental and theoretical vibrational spectrum of tautomer 3*

| Mode | Exp. / cm ⁻¹ | Theor. / cm ⁻¹ | Assignments |
|------|-------------------------|---------------------------|---|
| 42 | 3565 | 3490 | $\nu_{as} N_{10} H_{13,14}$ [95.0] |
| 41 | 3379 | 3372 | $\nu N_1 H_{15}$ [92.4] + $\nu_{as} N_{10} H_{13,14}$ [7.6] |
| 40 | 3300 | 3345 | $\nu N_1 H_{15}$ [96.2] |
| 39 | 3230 | 3288 | $\nu_{as} N_9 H_{11,12}$ [99.3] |
| 38 | 3177 | 3243 | $\nu_{as} N_9 H_{11,12}$ [98.8] |
| 37 | 2577 | 2517 | $\nu S_7 H_{16}$ [99.3] |
| 36 | 1647 | 1663 | $\delta N_9 H_{11,12}$ [62.8] + $\delta N_{10} H_{13,14}$ [20.3] + $\nu C_{4,5,6}$ [9.5] + $\nu_{as} N_1 C_2 N_3$ [7.3] |
| 35 | 1565 | 1628 | $(\delta N_{10} H_{13,14} + \nu C_4 N_{10})$ [57.6] + $\delta N_9 H_{11,12}$ [37.0] |
| 34 | 1525 | 1587 | $\delta N_{10} H_{13,14}$ [38.1] + $\delta N_9 H_{11,12}$ [25.2] + $\nu C_{4,5,6}$ [12.8] + $\nu_{as} N_1 C_2 N_3$ [19.7] + $\delta S_7 H_{16}$ [4.7] |
| 33 | 1462 | 1542 | $\pi N_1 H_{15}$ [56] + $\nu C_2 N_3 C_4$ [21.3] + $\delta N_9 H_{11,12}$ [17.1] + $\delta N_{10} H_{13,14}$ [13.0] + $\delta C_5 C_6 S_8$ [8.8] |
| 32 | 1430 | 1508 | $\delta C_{4,5,6}$ [40.0] + $\delta N_1 H_{15}$ [29.9] + $\delta N_{10} H_{13,14}$ [22.2] + $\nu N_2 C_3$ [7.8] |
| 31 | 1386 | 1460 | $\nu(C_4-N_{10} H_{13,14})$ [67.7] + $\nu_{as} N_1 C_2 N_3$ [16.5] + $\delta N_9 H_{11,12}$ [10.8] + $\nu C_{5,6}$ [5.7] |
| 30 | 1346 | 1340 | $\nu C_{4,5,6}$ [24.5] + $\delta N_1 H_{15}$ [22.5] + $\tau N_9 H_{11,12}$ [22.1] + $\delta N_3 C_2 S_8 H_{16}$ [18.3] + $\rho N_{10} H_{13,14}$ [12.8] |
| 29 | 1300 | 1285 | $(\nu C_5 N_9 + \delta N_9 H_{11,12})$ [33.0] + $\rho N_{10} H_{13,14}$ [24.6] + $\nu_{as} C_2 N_3 C_4$ [16.4] + $\delta N_1 H_{15}$ [15.9] + $\nu C_6 S_8$ [5.5] |
| 28 | 1276 | 1233 | $\tau N_9 H_{11,12}$ [67.0] + $\rho N_{10} H_{13,14}$ [12.3] + $\delta N_1 H_{15}$ [8.0] + $\delta C_2 S_7 H_{16}$ [4.8] |
| 27 | 1232 | 1211 | $\rho N_{10} H_{13,14}$ [33.5] + $\tau N_9 H_{11,12}$ [25.1] + $\pi N_1 H_{15}$ [20.9] + $\delta C_2 N_3 C_4$ [9.4] + $\delta S_7 H_{16}$ [4.8] |
| 26 | 1182 | 1142 | $(\nu C_6 N_1 + \delta N_1 H_{15})$ [53.1] + $(\nu C_5 N_9 + \nu N_9 H_{11,12})$ [26.6] + $\delta S_7 H_{16}$ [10.6] + $\nu C_2 N_3 C_4$ [7] |
| 25 | 1156 | 1071 | $\rho N_{10} H_{13,14}$ [46.1] + $\delta N_1 H_{15}$ [17.9] + $\nu C_2 N_3 C_4$ [11.5] + $\nu C_6 S_8$ [6.3] + $(\nu C_5 N_9 + \omega N_9 H_{11,12})$ [14.0] |
| 24 | 1015 | 1040 | $\rho N_{10} H_{13,14}$ [24.8] + $\omega N_9 H_{11,12}$ [22.8] + $\delta N_3 C_4 C_5$ [20.0] + $\delta C_2 N_1 C_6$ [16.8] + $\delta S_7 H_{16}$ [15.4] |
| 23 | 910 | 959 | $\delta S_7 H_{16}$ [44.6] + $\omega N_9 H_{11,12}$ [29.1] + $\rho N_{10} H_{13,14}$ [11.7] + $\nu C_2 N_3 C_4$ [10.1] |
| 22 | 863 | 935 | $\omega N_9 H_{11,12}$ [53.6] + $(\delta S_7 H_{16} + \nu N_1 C_2 N_3)$ [32.9] + $\rho N_{10} H_{13,14}$ [8.0] |
| 21 | 806 | 885 | $\omega N_9 H_{11,12}$ [44.1] + $\delta S_7 H_{16}$ [24.5] + $\nu C_2 N_3 C_4$ [21.3] + $\nu C_6 S_8$ [9.9] |
| 20 | 746 | 752 | $\pi N_1 C_2 C_3$ [40.2] + $\pi C_2 N_1 C_6$ [33.1] + $\tau N_9 H_{11,12}$ [25.7] |
| 19 | 712 | 725 | $\tau N_{10} H_{13,14}$ [30.2] + $\nu C_5 N_9$ [25.5] + $\delta N_1 C_5 S_8$ [23.6] + $\nu C_2 S_7$ [10] + $\nu C_4 N_3$ [10.0] |
| 18 | | 672 | $\pi N_1 H_{15}$ [56.7] + $\tau N_{10} H_{13,14}$ [11.8] + $\pi C_{4,5,6}$ [11.2] + $\pi S_7 H_{16}$ [11] + $\omega N_9 H_{11,12}$ [8.7] |
| 17 | | 646 | $\tau N_{10} H_{13,14}$ [58.5] + $\pi N_1 C_2 N_3$ [18.1] + $\omega N_9 H_{11,12}$ [13.9] + $\pi C_{4,5,6}$ [9.3] |
| 16 | 600 | 638 | $\tau N_{10} H_{13,14}$ [44.1] + $\pi N_1 C_2 N_3$ [30.3] + $\pi C_{4,5,6}$ [25.8] |
| 15 | | 592 | $(\pi N_1 H_{15} + \pi N_1 C_3 C_6)$ [65.8] + $\pi C_4 N_3 C_2$ [28.3] + $\pi S_7 H_{16}$ [5.8] |
| 14 | 571 | 569 | $\nu ring$ [41.1] + $\rho N_{10} H_{13,14}$ [33.4] + $\omega N_9 H_{11,12}$ [17.4] + $\delta S_7 H_{16}$ [7.9] |
| 13 | 545 | 540 | $\rho N_{10} H_{13,14}$ [36.9] + $\delta ring$ [23.1] + $\omega N_9 H_{11,12}$ [18.0] + $\delta N_1 H_{15}$ [14.7] + $\delta S_7 H_{16}$ [7.2] |
| 12 | 495 | 442 | $\delta ring$ [55.9] + $\nu C_6 S_8$ [16.0] + $\delta N_1 H_{15}$ [14.8] + $\delta S_7 H_{16}$ [13.0] |

*Fractional composition of the vibrational modes are shown in parenthesis

dithiol structure. The characteristic $\nu(\text{N-H})$ vibrational peaks expected for this isomer at 3521, 3387, 3319 at 3261 cm^{-1} (Table 2), practically coincide with the experimental bands observed at 3565, 3379, 3300 and 3230 cm^{-1} for DADMcp. The $\nu(\text{S-H})$ vibrations appear as weak bands in the theoretical spectrum of isomer **1**, at 2678 and 2662 cm^{-1} (about 2% relative intensity), corresponding to the weak shoulders observed at 2693 and 2577 cm^{-1} , respectively.

In the case of the tautomer **2**, which corresponds to the dithione form, the $\nu(\text{N-H})$ vibrations are very close to those of tautomer **1**, however there is no (S-H) band (Table 3). Unfortunately, in this case, the $\nu(\text{C}=\text{S})$ vibration does not correspond to a characteristic peak, since it always occurs in combination with $\nu(\text{C-N})$ and $\nu(\text{C-C})$ vibrations, e.g. at 1294 cm^{-1} , in Table 2.

In the case of tautomer **3**, because of its mixed thiol and thione features, its theoretical vibrational spectrum exhibits a close similarity with those of tautomers **1** and **3**, as shown in Table 4.

Therefore, one can see that the infrared spectra fit fairly well those predicted by the theoretical model, corroborating the existence of a mixture of tautomers.

Additional evidence for the occurrence of the thiol tautomers (**1** or **3**) was obtained from the near-infrared (NIR) spectrum of the DADMcp species, as shown in Figure 4. In fact, it should be mentioned that the NIR region is being increasingly exploited in analytical chemistry, because of the occurrence of characteristic overtone and combination bands of the C-H, N-H, O-H and S-H fundamental vibrations. In the DADMcp compound, only the N-H and S-H vibrations³⁰ can contribute to the NIR spectrum, occurring at frequencies approximately two times those observed for the fundamental ones in the middle IR region, *i.e.*, at 6653, 6473, 6293 and 4968, 4778 cm^{-1} , respectively (Figure 4).

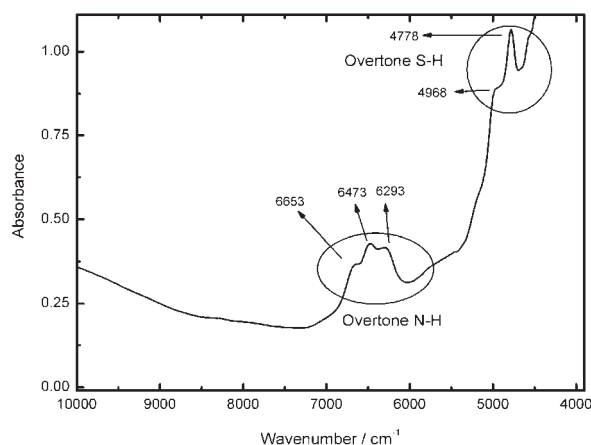


Figure 4. NIR spectrum of 4,5-diamine-2,6-dimercaptopyrimidine in solid form.

Conclusions

Due to the thione–thiol equilibrium, the 4,5-diamine-2,6-dimercaptopyrimidine compound can exhibit nine tautomeric forms. HF/SCF and DFT calculations support the existence of at least two major tautomeric forms of which the dithione tautomer is the most stable one. A successful simulation of the vibrational spectra of the most stable tautomers is reported, showing a good agreement with the experimental bands in the FTIR spectrum. According to the theoretical and experimental evidence, tautomers **2** and **3** should be the predominant species in the solid state. This conclusion is corroborated by the S-H overtone band, in the NIR spectrum.

Acknowledgments

The support from FAPESP, CNPq, and IM2C is gratefully acknowledged.

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Received: October 9, 2007

Published on the web: February 22, 2008

FAPESP helped in meeting the publication costs of this article.