

Spectrochimica Acta Part A 52 (1996) 645-659

SPECTROCHIMICA ACTA PART A

Infrared spectra of 6-azathiouracils: an experimental matrix isolation and theoretical ab initio SCF/6-311G** study

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Received 15 August 1995; accepted 19 October 1995

Abstract

The infrared (IR) absorption spectra of 2-thio-6-azauracil, 4-thio-6-azauracil and 2,4-dithio-6-azauracil isolated in low-temperature Ar and N₂ matrices are reported. These compounds have been found to exist in low-temperature matrices exclusively in the oxothione and dithione tautomeric forms. An assignment of the observed infrared bands is proposed on the basis of comparison of the experimental matrix spectra with the spectra calculated at the ab initio SCF/6-311G** level. The IR spectra of the title compounds are compared with the previously published IR spectra of matrix isolated 2-thiouracil, 4-thiouracil and 2,4-dithiouracil.

Keywords: Ab initio; Azathiouracil; Infrared; Matrix isolation

1. Introduction

Thiouracils and 6-azauracils are the analogues of the parent nucleic acid base uracil; both groups of compounds are well known due to their presence in biological material and pharmacological activities. Thiouracils were found in RNA in the late 1960s [1,2]. The role of 4-thiouridine in crosslinking m-RNA to r-RNA and to proteins is currently under intense study [3,4]. 6-Azauracil has been clinically applied as an antitumour drug. 6-Azauridine was found to inhibit both DNA and RNA synthesis [5]. 2-Thio-6-azauridine is active both in vitro and in vivo against mouse L1210 leukemia cells and 2-thio-6-azauridine 5'monophosphate is a potent inhibitor of orotidine decarboxylase [6] similarly to the 5'-monophosphate of 6-azauridine [7]. Introduction of sulphur into the 4-position of 6-azauracil diminishes bacteriostatic activity by one order of magnitude, but 4-thio-6-azauridine was found to be significantly more active than unsubstituted 6-azauridine [8].

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Their biological activity was the motivation for the present study of some physicochemical characteristics of 6-azathiouracils. In the present work the infrared (IR) spectra of three 6-azathiouracils (2-thio-6-azauracil, 4-thio-6-azauracil and 2,4dithio-6-azauracil) have been investigated by the matrix isolation technique and ab initio quantum chemical calculations.

2. Experimental

The method of matrix preparation was similar to that described elsewhere [9]. The sample (purified by vacuum sublimation before the matrix experiment) was placed in a microoven in the vacuum chamber of a continuous-flow helium cryostat. The vapours of the sample emitted from the heated microoven were mixed with matrix gas (Ar or N_2 precooled in a liquid nitrogen trap) and deposited on a CsI window on the cold finger (10 K) of the cryostat. The matrix gases, argon (Linde AG) and nitrogen (Technische Gase, Leipzig), were of purity grade 6.0. The sample was sublimed at oven temperatures of 365 K (2-thio-6azauracil), 350 K (4-thio-6-azauracil) and 340 K (2,4-dithio-6-azauracil). The IR spectra were recorded with Perkin-Elmer 580B spectrometer operating at 1-3 cm⁻¹ resolution. Integral intensities of the absorption bands were measured by numerical integration.

The compounds studied in this work were prepared starting from commercially available 6-azauracil. Thiation of 6-azapyrimidinones has hitherto been based largely on the use of P_4S_{10} in pyridine [10,11] or in other high boiling solvents such as tetrahydronaphthalene [10]. The use of refluxing pyridine leads mainly to thiation of the 4-keto group of 6-azauracil(s) [11] with a very small yield of 2,4-dithio-6-azapyrimidine [10]. The more potent Lawesson thiation reagent has received less attention, but it has been employed successfully in our laboratory for synthesis of thiated analogues of pyrimidines [12]. The yields of 2,4-dithio derivatives obtained were high. Therefore a study on the thiation of 6-azapyrimidinones using this procedure was undertaken. The reaction of 6-azauracil with an equimolar amount of the Lawesson reagent (under reflux in anhydrous 1,4-dioxane) resulted in complete conversion (monitored by thin-layer chromatography (TLC)) to 4-thio-6-azauracil. Thiation of the 2keto group proceeded less readily. However, prolongation of the reaction time in the presence of two or more molar equivalents of the Lawesson reagent led to the desired 2,4-dithio derivative with a good yield (90%). To our knowledge this is the first example of successful thiation of the 2-keto group in 6-azauracil by use of the Lawesson reagent.

2.1. Synthesis of 4-thio-6-azauracil

To a solution of 6-azauracil (1.13 g, 10 mmol) in 50 ml anhydrous 1,4-dioxane the Lawesson reagent (2.25 g, 5.57 mmol) was added. The mixture was heated under reflux for 2 h with exclusion of moisture, while the progress of the reaction was monitored by TLC in the mixture CHCl₃:MeOH 95:5 (solvent A). Dioxane was removed under vacuum and the residual oil was dissolved in boiling water. Insoluble material was removed by filtration and the clear filtrate was stored for crystallisation. The product was recrystallised from ethanol to give 1.01 g 4-thio-6-azauracil. Yield, 89%; m.p., 216–217°C (lit. 213–214°C [10]); TLC, $R_{\rm F}$ is 0.43 in solvent A.

2.2. Synthesis of 2,4-dithio-6-azauracil

To a solution of 6-azauracil (1.017 g, 9 mmol) in 60 ml anhydrous 1,4-dioxane the Lawesson reagent (10.908 g, 26.16 mmol) was added. The mixture was heated under reflux for 24 h with exclusion of moisture, while the progress of the reaction was monitored by TLC in solvent A. The cooled reaction mixture was brought to an oil under vacuum, taken up with 50 ml water and extracted three times with 20 ml portions of ethyl acetate. The ethyl acetate extracts were combined and concentrated under vacuum. Next the crude product was dissolved in boiling 2-butanol, filtered, and left for crystallisation. An analytical sample was obtained by recrystallisation from ethanol to give 760 mg 2,4-dithio-6-azauracil. Yield, 90%; m.p., 207-208°C (lit. 209-210°C [10]), TLC; $R_{\rm F}$ is 0.72 in solvent A.

2.3. Synthesis of 2-thio-6-azauracil

This compound was previously prepared by cyclisation of the thiosemicarbazone of the glyoxylic acid [13]. Another multistep synthesis was based on the decarboxylation of 3-mercapto-5-hydroxy-1,2,4-triazine-6-carboxylic acid which was prepared by condensation of diethyl oxomalonate with thiosemicarbazide and cyclisation of resulting thiosemicarbazone [10]. In the present work 2-thio-6-azauracil was obtained by acid-catalysed deamination of 2-thio-6-azacytosine. The latter compound was prepared from 2,4-dithio-6-azauracil according to the procedure of Fu et al. [14]. 2-Thio-6-azacytosine $(m.p. > 300^{\circ}C;$ lit. value $> 300^{\circ}$ C [13]) was obtained with a yield of 85%. A solution of 3 g (26.3 mmol) 2-thio-6-azacytosine in 300 ml 0.6 M HCl was heated for 20 h at 37°C. The reaction mixture was brought to dryness several times from toluene, and the residue was crystallised from methanol to obtain 2.1 g (67%) of 2-thio-6-azauracil (the yield based on 6-azauracil was 52%); m.p. 230-231°C (lit. value 227–228°C [10]); TLC, $R_{\rm F}$ is 0.49.

Melting points (uncorrected) were determined with the Boetius microscope hot stage; TLC was carried out on Merck 60 F_{251} silica gel plates (DC, 0.25 mm, No. 5715) and preparative (PSC, 2 mm, No. 5717) plates. 1,4-Dioxane was purified by passage through a column of Merck alkaline Al₂O₃ (Brockman activity I) and stored over 4 Å molecular sieves. The Lawesson reagent was purchased from Aldrich.

3. Computational

The optimisation of the geometry of the studied 6-azathiouracils, in their oxothione or dithione tautomeric forms, was performed at the SCF/6-311G** level of theory with the use of the gradient procedures of the GAUSSIAN 92 program [15]. Next the harmonic vibrational frequencies and the IR intensities were calculated at the same level of theory. In order to approximately correct for the electronic correlation, the basis set truncation and the vibrational anharmonicity effects, the calculated wavenumbers of all normal modes were scaled down by a single factor of 0.9. The theoretically calculated force constant matrices in the Cartesian coordinates were transformed to the molecule fixed internal coordinates in order to enable the standard PED analysis [16] of the normal modes. The atom numbering is shown in Scheme 1 and the internal coordinate set used in the PED calculation is given in Table 1. For the sake of better presentation of the normal mode forms in the 2,4-dithio-6-azauracil molecule the PED analysis was also performed using an altered set of internal coordinates. These coordinates correspond to in-phase and out-of-phase coupled stretching, bending and wagging vibrations of the C2=S and C4=S groups. For similar reasons, for the three studied compounds, the bending vibrations of the NH groups are also presented in the terms of the in-phase and out-of-phase vibrations.

4. Results and discussion

The IR spectra of 2-thio-6-azauracil (2T6AU), 4-thio-6-azauracil (4T6AU), 2,4-dithio-6-azauracil (24DT6AU) isolated in Ar and N_2 matrices are presented in Figs. 1, 2 and 3, respectively. These spectra are compared with the results of the theoretical simulations which are presented in the



X = S, Y = O 2-thio-6-azauracil X = O, Y = S 4-thio-6-azauracil X = S, Y = S 2,4-dithio-6-azauracil

Scheme 1. Atom numbering for the studied 6-azathiouracils.

Table 1

| $S_1 = r_{1,2}$ | vN1C2 |
|--|----------------------|
| $S_2 = r_{2,3}$ | vC2N3 |
| $S_3 = r_{3,4}$ | vN3C4 |
| $S_4 = r_{4,5}$ | vC4C5 |
| $S_5 = r_{5,6}$ | vC5N6 |
| $S_6 = r_{6,1}$ | vN6N1 |
| $S_7 = r_{1,11}$ | vN1H |
| $S_8 = r_{3,9}$ | vN3H |
| $S_9 = r_{5,10}$ | vC5H |
| $S_{10} = r_{2.7}$ | vC2X |
| $S_{11} = r_{4,8}$ | vC4Y |
| $S_{12} = (6^{-1/2})(\beta_{2,6,1} - \beta_{1,3,2} + \beta_{4,2,3} - \beta_{5,3,4} + \beta_{6,4,5} - \beta_{5,1,6})$ | $\beta R1$ |
| $S_{13} = (12^{-1/2})(2\beta_{2,6,1} - \beta_{3,1,2} - \beta_{4,2,3} + 2\beta_{3,5,4} - \beta_{6,5,4} - \beta_{1,5,6})$ | βR2 |
| $S_{14} = 1/2(\beta_{1,3,2} - \beta_{2,4,3} + \beta_{4,6,5} - \beta_{1,5,6})$ | $\beta R 3$ |
| $S_{15} = 1/2(\beta_{11,6,1} - \beta_{11,2,1} + \beta_{9,2,3} - \beta_{9,4,3})$ | βNH in-ph |
| $S_{16} = 1/2(\beta_{11,6,1} - \beta_{11,2,1} - \beta_{9,2,3} + \beta_{9,4,3})$ | β NH out-of-ph |
| $S_{17} = (2^{-1/2})(\beta_{7,1,2} - \beta_{7,3,2})$ | βC2X |
| $S_{18} = (2^{-1.2})(\beta_{8,3,5} - \beta_{8,5,4})$ | βC4Y |
| $S_{19} = (2^{-1/2})(\beta_{10,4,5} - \beta_{10,6,5})$ | βC5H |
| $S_{20} = (6^{-1/2})(\tau_{1,2,3,4} - \tau_{2,3,4,5} + \tau_{3,4,5,6} - \tau_{4,5,6,1} + \tau_{5,6,1,2} - \tau_{6,1,2,3})$ | τ R 1 |
| $S_{21} = 1/2(\tau_{1,2,3,4} - \tau_{3,4,5,6} + \tau_{4,5,6,1} - \tau_{6,1,2,3})$ | τ R 2 |
| $S_{22} = (12^{-1/2})(-\tau_{1,2,3,4} + 2\tau_{2,3,4,5} - \tau_{3,4,5,6} - \tau_{4,5,6,1} + 2\tau_{5,6,1,2} - \tau_{6,1,2,3})$ | τ R 3 |
| $S_{23} = \gamma_{11.6,1,2}$ | 7'N1H |
| $S_{24} = \gamma_{9,2,3,4}$ | γ N3H |
| $S_{25} = \gamma_{7,1,2,3}$ | ?'C2X |
| $S_{26} = \gamma_{8,3,4,5}$ | 7°C4Y |
| $S_{27} = \gamma_{10,4,5,6}$ | γC5H |

Internal coordinates used in the normal modes analysis for 2-thio-6-azauracil, 4-thio-6-azauracil and 2,4-dithio-6-azauracil (atom numbering as in Scheme 1)^{a,b}

^a $r_{i,j}$ is the distance between atoms A_i and A_j ; $\beta_{i,j,k,l}$ is the angle between vectors $A_k A_l$ and $A_k A_j$; $\gamma_{i,j,k,l}$ is the angle between the vector $A_k A_l$ and the plane defined by atoms A_j , A_k , A_l ; $\tau_{i,j,k,l}$ is the dihedral angle between the plane defined by A_i , A_j , A_k and the plane defined by A_i , A_j , A_k and the plane defined by A_i , A_j , A_k and the plane defined by A_i , A_j , A_k and the plane defined by A_i , A_j , A_k and the plane defined by A_i , A_j , A_k , A_j atoms.

^b For 2-thio-6-azauracil X is S and Y is O: for 4-thio-6-azauracil X is O and Y is S; and for 2,4-dithio-6-azauracil X is S and Y is S.

"stick spectrum" form. The frequencies and intensities of the experimentally observed and theoretically predicted bands in the IR spectra of all studied compounds are collected in Tables 2–4. The proposed assignment is also shown in these tables. Many common features were found in the spectra of the compounds studied in the present work. These similarities will be discussed in this section together with a comparison of the spectra of 2T6AU, 4T6AU and 24DT6AU with the spectra of 2-thiouracil (2TU), 4-thiouracil (4TU) and 2,4-dithiouracil (24DTU) studied previously by Rostkowska et al. [17] and Graindourze et al. [18].

In the high frequency region 4000-2000 cm⁻¹, two bands due to stretching vibrations of N1H and N3H are observed at the frequencies 3480-

3430 cm⁻¹ and 3410–3385 cm⁻¹, respectively. The assignment of the band at higher frequency to the vN1H mode and of the band at lower frequency to the vN3H mode is in agreement with the theoretical calculations performed in this work. It is also supported by the detailed analysis of this region in the spectra of 2TU and 4TU [17,18] using N-methylated model compounds. In all the studied compounds the band due to the N1H stretching has a higher intensity than the band due to the N3H stretching which is also in agreement with the theoretical prediction. By comparing the spectral positions of the vNH bands in the spectra of 6-azathiouracils with the spectral positions of those bands in the IR spectrum of 6-azauracil (6AU) [19] (which are 3476,



Fig. 1. The infrared spectra of 2-thio-6-azauracil: curves A, spectra theoretically simulated at the SCF/6-311G** level; curves B, experimental spectra of 2T6AU isolated in N_2 matrix.

3470 cm⁻¹ (AR) for ν N1H and 3423 cm⁻¹ (AR) for ν N3H), we conclude that the replacement of an oxygen atom by sulphur leads to a shift of the

vNH bands to lower frequencies. This shift is very small if the C=S group is not placed in the direct vicinity of the NH group. This is the case for the



Fig. 2. The infrared spectra of 4-thio-6-azauracil: curves A, spectra theoretically simulated at the SCF/6-311G^{**} level; curves B, experimental spectra of 4T6AU isolated in Ar matrix; curves C, experimental spectra of 4T6AU isolated in N₂ matrix.



Fig. 3. The infrared spectra of 2,4-dithio-6-azauracil: curves A, spectra theoretically simulated at the SCF/6-311G** level; curves B, experimental spectra of 24DT6AU isolated in Ar matrix; curves C, experimental spectra of 24DT6AU isolated in N_2 matrix.

band due to ν N1H, which is shifted in the spectrum of 4T6AU by only 1-4 cm⁻¹ with respect to the position of the corresponding band in the

spectrum of 6AU. If, however, the C=S group is in the direct vicinity of the NH group, then the shift of the vNH band is more pronounced and

Table 2

The experimental wavenumbers (\tilde{v}) , integral intensities (1) and assignments to the normal modes (Q) of the bands observed in Ar and N₂ matrices compared with theoretically calculated wavenumbers, absolute intensities (Ath) and potential energy distribution (PED) of the absorption bands of 2-thio-6-azauracil^{a,b}

| Mode | Experim | ental | | | Calcula | ted SCF/6-311 | G** |
|------|--------------------------------|-------------|--------------------|-----------------|-------------------------|---|--|
| no. | Ar matr | ix | N ₂ mat | rix | | | |
| | $\overline{\tilde{v}/cm^{-1}}$ | I (rel.) | \vec{v}/cm^{-1} | <i>I</i> (rel.) | v⊄/ cm ^{−1} | A ^{.th} / (km mol ⁻¹) | PED/%) |
| Q1 | 3453 | 234 | 3436 | 308 | 3497 | 136 | ۶N1H (100) |
| Q2 | 3406 | 153 | 3388 | 213 | 3443 | 105 | vN3H (100) |
| õ3 | | | | | 3043 | 0.1 | vC5H (99) |
| ~ | 1857 | 5 | | | | | |
| | 1851 | 8 | | | | | |
| | 1759 | 15 | | | | | |
| 04 | 1747 | 525 | 1745 | 446 | 1814 | 710 | vC4O (81) |
| Υ. | 1717 | 97 | 1722 | 164 | 1011 | /10 | |
| | 1696 | 12 | 1700 | 23 | | | |
| | 1610 | 0 | 1508 | 23 | | | |
| 05 | 1010 | 0 | 1590 | 5 | 1670 | 2 | "C5N(4 (77) |
| QS | 1588 | 13 | 1591 | 15 | 10/9 | 3 | VCSINO(77) |
| | 1531 | 27 | 1535 | 11 | | | |
| | 1515 | | 1524 | | | | |
| Q6 | 1508 > | 739 | 1515 } | 702 | 1542 | 749 | β NH out-of-ph (63) |
| | 1504 J | | 1507 J | | | | |
| | 1496 | 4 | 1495 | 10 | | | |
| | 1489 | 30 | | | | | |
| | 1481 | 8 | | | | | |
| Q7 | 1441 | 8 | 1470 | 13 | 1420 | 41 | β NH in-ph, vC2N3 (13) |
| Q8 | 1402 | 92 | 1399 | 94 | 1395 | 191 | ν N1C2 (23), β NH in-ph (20), ν C2N3 (16), ν N3C4 (12) |
| | 1382 | 5 | 1396 | sh | | | |
| | 1374 | 53 | 1381 | 8 | | | |
| | 1366 | 16 | 1365 | 12 | | | |
| | 1354 | 12 | | | | | |
| 09 | 1330 | 49 | 1333 | 16 | 1320 | 57 | β C5H (59), vN6N1 (10) |
| ~ | 1324 | 24 | 1329 | 13 | | | |
| | 1319 | 8 | | | | | |
| | 1282 | 6 | 1294 | 5 | | | |
| | 1227 | 3 | | - | | | |
| 010 | 1245 | 50 | 1249 | 80 | 1241 | 63 | $vN3C4$ (27) $\betaC5H$ (22) $vC2N3$ (13) $vN3C4$ (11) |
| 210 | 1272 | 31 | 1217 | 00 | 12.11 | 0.5 | |
| | 1104 | 1 | | | | | |
| | 1174 | 4 | 1171 | 192 | | | |
| 011 | 1165 | 212 | 1147 | 165 | 1149 | 410 | $\beta P (22) = \beta N H$ out of $ph(16) = pC (16) = nN1C 2$ |
| QΠ | 1105 | 515 | 1102 | 109 | 1140 | 412 | ρ K1 (25), ρ NH out-of-ph (16), ν C25 (16), ν NTC2 (14), ν N6N1 (13) |
| | 1150 | 15 | 1146 | 2 | | | |
| | 1136 | 11 | 1137 | 10 | | | |
| 012 | 1053 | 13 | 1055 | 10 | | | |
| Q12 | 1029 | 18 | 1048 | 10 | 1048 | 47 | ν N6N1 (53), ν C2S (16), β R1 (10) |
| Q13 | 1003 | 26 | 1017 | 29 | 1007 | 50 | β R1 (41), ν N1C2 (26), ν C2N3(17) |
| | | | 886 | sh | | | |
| Q14 | 878 | 22 | 882 | 37 | 910 | 22 | γC5H (101), γC4O (13) |
| Q15 | 928 | 14 | 924 | 28 | 901 | 2 | vN3C4 (34), vC4C5 (24), v C2S (16) |
| Q16 | 745 | 14 | 753 | 40 | 755 | 33 | γC4O (58), τR1 (24), γN3H (18) |
| Q17 | 695 | 157 | 721 | 137 | 694 | 154 | γN3H (75), τR1 (24) |
| - | | | 718 | sh | | | |

Table 2 (continued)

| Mode | Experim | ental | | | Calculat | ted SCF/6-311C | ;** |
|------------------|------------|--------------------|--------------------------|-------------|-----------------------------|--|--|
| no. | Ar matr | ix | N ₂ matri | x | | | |
| | ĕ∉ cm ⊥ | <i>I</i> (rel.) | ₽́/ cm ⁺⁺¹ | I (rel.) | - €/ cm ⁻¹ | A th / (km mol ^{−1}) | PED % |
| Q18 | 685 | 17 | 686 | 14 | 670 | 18 | ν C4C5 (33), β R2 (29), ν C2S (12) |
| \tilde{Q} 19 | | | | | 637 | 1 | γC2S (43), τR2 (12), γN3H (10) |
| - | | | 654 | 29 | | | |
| Q20 | 611 | 14 | 633 | 23 | 613 | 61 | 7N1H (85), 7C2S (31) |
| $\overline{Q}21$ | 539 | 40 | 524 | 38 | 534 | 29 | β R2 (71) |
| Q22 | 477 | 30 | 479 | 30 | 474 | 29 | β C4O (53), β R3 (20), β C2S (13) |
| Q23 | 452 | 11 | 452 | 12 | 437 | 20 | $\nu C2S$ (37), $\beta R3$ (27) |
| Q24 | | | | | 418 | 0.002 | $\tau R3$ (31), $\tau R2$ (24), $\gamma C4O(23)$, $\tau R1(17)$ |
| Q25 | 268 | 12 | 272 | 9 | 265 | 10 | β C2S (72), β C4O (10) |
| Q26 | | | | | 148 | 2 | $\tau R3$ (54), $\tau R2$ (52) |
| Q27 | | | | | 131 | 3 | $\tau R1$ (48), $\tau R3$ (25), $\tau R2$ (23) |

^a Theoretical positions of absorption bands were scaled by the factor 0.9; PEDs lower than 10% not included.

^b Abbreviations: *I*, Integral absorbances of absorption bands normalised in such a way that the observed intensity sum of all modes is equal to the calculated intensity sum of all modes; A^{th} , calculated intensities; rel., relative; sh, shoulder; ν , β , τ , γ are defined in Table 1.

reaches 15-24 cm⁻¹. This kind of behaviour may be observed, for example, in the vN3H bands in the spectra of 4T6AU and 2T6AU or in the vN1H bands in the spectra of 2T6AU and 24DT6AU. In 24DT6AU the N3H group is in close proximity to both C=S groups and their combined interaction lowers the vN3H band position by more than 30 cm⁻¹ with respect to the wavenumber of this band in the spectrum of 6AU.

No bands were observed in the regions $3650-3550 \text{ cm}^{-1}$ and $2650-2550 \text{ cm}^{-1}$, where the bands due to vOH and vSH could be expected. This indicates that in low temperature matrices 2T6AU and 4T6AU exist (like 2TU and 4TU) exclusively in the oxothione forms and that 24DT6AU exists (like 24DTU) exclusively in the dithione form.

In the spectra of 2T6AU and 4T6AU very strong, multiply split bands due to the ν C=O stretching vibrations are present in the spectral region 1780–1680 cm⁻¹. Such a splitting, probably caused by the Fermi resonance, is characteristic for the ν C=O bands in the spectra of uracils [19,20] and thiouracils [17,18]. As expected no absorption was found in the 1780–1680 cm⁻¹ region in the spectrum of 24DT6AU. The bands due to stretching vibrations of double bond in the ring, C5=N6,

were found in the experimental spectra at 1588 cm⁻⁺ (for 2T6AU), 1581 cm⁻⁺ (for 4T6AU) and 1588 cm⁻¹ (Ar) (for 24DT6AU). In the spectrum of 6AU an analogous band was observed at 1594 cm^{-1} (Ar). In the spectra of 2TU, 4TU and 24DTU bands due to the stretching of the C5=C6 double bond were observed at frequencies which were higher by about 50 cm⁻¹ [17,18]. As was pointed out by Rostkowska et al. [17] the intensity of these bands changes considerably from one compound to the other. In the spectrum of 4T6AU the band is intense, while for 2T6AU it is weak, and for 24DT6AU it has an intermediate intensity. This pattern of intensity change is similar to that previously observed in the series 4TU, 2TU and 24DTU.

The bending vibrations of the N1H and N3H groups are coupled in all the 6-azathiouracils considered. The band corresponding to the normal mode resulting from the out-of-phase coupling of those vibrations is very strong and appears at 1508 cm⁻¹, 1457 cm⁻¹ and 1515 cm⁻¹ (Ar) in the spectra of 2T6AU, 4T6AU and 24DT6AU, respectively. Analogous strong bands in the spectra of 2TU and 24DTU were found at 1541 cm⁻¹ (N₂) and 1540 cm⁻¹ (N₂) [17]. The

Table 3

The experimental wavenumbers (\hat{v}) , integral intensities (I) and assignments to the normal modes (Q) of the bands observed in Ar and N₂ matrices compared with theoretically calculated wavenumbers, absolute intensities (Ath) and potential energy distribution (PED) of the absorption bands of 4-thio-6-azauracil^{a,b}

| Mode | Experir | nental | | | Calcula | ited SCF/6-3110 | G** |
|---------------|-----------------------|-------------|--------------------------------|-------------|--------------------------|--|--|
| no. | Ar mat | rix | N ₂ mat | rix | | | |
| | ₹ cm ^{−1} | / (rel.) | ũ / cm ^{−1} | I (rel.) | ₽̃/ cm ^{- 1} | A th / (km mol ⁻¹) | PED/% |
| | 3478 | | | | | | |
| Ψ | 3466 | 355 | 3451 | 445 | 3499 | 172 | vN1H (100) |
| 02 | 3408 | 144 | 3390 | 221 | 3442 | 92 | vN3H (100) |
| \tilde{o}_3 | | | | | 3057 | 3 | vC5H (99) |
| 2 | | | 1898 | 10 | | | |
| | | | 1852 | 5 | | | |
| | | | 1831 | 6 | | | |
| | 1815 | 17 | 1821 | 4 | | | |
| | 1015 | | 1778 | sh . | | | |
| | | | 1772 | 011 | | | |
| 04 | 1773 | 868 | 1763 | 1071 | 1802 | 1065 | vC2O (75) |
| 2' | 1768 | sh | 1750 | sh | | 1000 | |
| | 1758 | 106 | 1746 | 511 | | | |
| | 1744 | 98 | 1731 | 8 | | | |
| | 1716 | 9 | 1716 | 8 | | | |
| | 1710 | | 1694 | 4 | | | |
| | | | 1635 | 2 | | | |
| | 1600 | 17 | 1509 | 24 | | | |
| 05 | 1600 | 144 | 1590 | 102 | 1450 | 105 | $(C5N) \in (77)$ |
| Q^{5} | 1501 | 15 | 1360 | 105 | 1059 | 195 | |
| | 1575 | 15 | 1576 | 22 | | | |
| | 1512 | 16 | 1510 | 22 | | | |
| | 1515 | 0 | 1510 | 23 | | | |
| | 1402 | 0 | | | | | |
| 06 | 1492 | 45 | 1467 | 102 | 1496 | 202 | β NH out of ph (54) μ N3C4 (17) μ C2O (13) |
| Q0 | 1437 | 109 | 1407 | 195 | 1400 | 502 | β NH in ph (66) wN6N1 (10) |
| Q^{\prime} | 1432 | .04 10 | 1430 | 2 | 1440 | / | p with in-pit (00), v wolwit (10) |
| | 1360 | 20 | 1276 | 2 5 | | | |
| 09 | 1308 | 20 | 13/0 | 3 | 1272 | 70 | |
| Q_8 | 1330 | 20 | 1369 | 74 | 1372 | 12 | V(4C3 (10), V(1)C2 (10), V(1)SC4 (13), V(2)N3 (11) |
| 00 | 1338 | 20 | 1339 | 34 | 1220 | 15 | $\partial GSU(G2) = \partial NU(G2) = \partial F(11)$ |
| Q9 | 1325 | /0 | 1330 | 40 | 1338 | 45 | $\rho C S H (62), \rho N H III-ph (11)$ |
| | 1273 | 10 | 1202 | 10 | | | |
| 010 | 1264 | 10 | 1283 | 10 | 1250 | 250 | NICA (20) CONIA (10) NIACO (14) |
| Q10 | 1257 | 136 | 1260 | 137 | 1250 | 250 | ν N3C4 (28), ν C2N3 (19), ν N1C2 (14) |
| | 1249 | 53 | 1254 | 51 | | | |
| | | | 1217 | 48 | | | |
| | 1179 | 8 | | | | | |
| | 1174 | 8 | | | | | |
| Q^{11} | 1167 | 137 | 1164 | 110 | 1146 | 185 | ν C4S (29), β R1 (24), β C5H (13), ν N6N1 (10) |
| | 1113 | 8 | | _ | | | |
| | 1103 | 8 | 1117 | 7 | | | |
| Q12 | 1087 | 168 | 1092 | 155 | 1095 | 320 | vN6N1 (47), vC4S (12), vN1C2 (12) |
| | 1067 | 13 | 1072 | 39 | | | |
| | 1050 | 6 | | | | | |
| Q13 | 1006 | 3 | 1014 | 6 | 985 | 8 | β R1 (52), vC4C5 (21), vN3C4 (14) |
| | 957 | 10 | | | | | |
| Q14 | 937 | 15 | 949 | 19 | 932 | 17 | vC2N3 (36), vN1C2 (26), vC4S (12) |

Table 3 (continued)

| Mode | Experim | ental | | | Calculat | ed SCF/6-311G* | ** |
|----------------|------------|-------------|---------------------|-------------|-------------------------|---|--|
| no. | Ar matr | ix | N ₂ matr | ix | | | |
| | ṽ/ cm−t | I (rel.) | \tilde{v}/cm^{-1} | / (rel.) | ₿/ cm ^{≈ 1} | A^{th} . (km mol ¹) | PED/% |
| 015 | 885 | 10 | 890 | 5 | 903 | 9 | ;;С5Н (109) |
| Q16 | 746 710 | 60 9 | 753 | 82 | 771 | 83 | ; C2O (95), ; N3H (16) |
| Q17 | 688 | 163 | 711 687] | 106 | 690 | 98 | γN3H (58), τR1 (45) |
| Q18 | 669 | 3 | 683 | 35 | 672 | 10 | νC4C5 (21), βR2 (19), νN1C2 (14), νC4S (12), νN6N1 (11) |
| Q19 | | | | | 666 | 1 | γ C4S (43), γ N3H (33), τ R2 (14), τ R1 (13) |
| \tilde{Q} 20 | | | 606 | 70 | 563 | 85 | 7N1H (86), 7C4S (11) |
| - | 566 | 104 | | | | | |
| Q21 | | | 568 | 23 | 563 | 20 | $\beta R3$ (72) |
| Q22 | 489 | 38 | 493 | 39 | 492 | 24 | β C2O (63), β C4S (14), β R2 (11) |
| Q23 | 435 | 25 | 435 | 19 | 424 | 22 | β R2 (43), vC4S (29), vC2N3 (10) |
| \tilde{Q} 24 | 381 | 11 | 391 | 3 | 386 | 7 | $\tau R3$ (33), $\gamma C4S$ (32), $\tau R2$ (18), $\gamma N1H$ (12) |
| Q25 | 267 | 12 | 271 | 8 | 266 | 11 | β C4S (75) |
| Q26 | | | | | 156 | 0.01 | $\tau R2$ (74), $\tau R1$ (32) |
| Q27 | | | | | 119 | 3 | $\tau R3$ (71), $\tau R1$ (20) |

^a Theoretical positions of absorption bands were scaled by the factor 0.9; PEDs lower than 10% not included.

^b Abbreviations: *I*, integral absorbances of absorption bands normalized in such a way that the observed intensity sum of all modes is equal to the calculated intensity sum of all modes; A^{th} , calculated intensities; rel., relative; sh. shoulder: ν , β , τ , γ are defined in Table 1.

strong band due to the β NH vibrations was observed in the spectrum of 4TU at considerably lower frequency, 1455 cm⁻¹ (Ar) [17], just as in 4T6AU. Contrary to the β NH out-of-phase bands, the bands due to the in-phase bending vibrations of the NH groups (Q7 in the spectra of 2T6AU and 4T6AU, and Q6 in the spectrum of 24DT6AU) have much lower intensities.

The band corresponding to the β C5H vibration appears, in the spectra of the three considered 6-azathiouracils, at nearly the same frequency, 1330–1325 cm⁻¹. In all three spectra its intensity is intermediate.

Very strong bands are observed in the range 1200-1100 cm⁻¹ for all three studied 6-azathiouracils. These bands correspond to normal modes in which the stretching vibrations of the C=S groups are involved. The ν C=S vibrations are always coupled in these modes with a ring stretching or with ring trigonal deformation vibrations. For the Q11 mode of 24DT6AU, corresponding to a very strong band at 1113 cm⁻¹ (Ar), the theoretical calculations predict some out-of-phase coupling of the two C=S stretching vibrations. Very strong bands due to normal modes involving ν C=S vibrations were previously observed [17,18] at very similar frequencies for 2TU, 4TU and 24DTU.

The bands corresponding to the normal modes involving out-of-plane wagging vibrations of the NH groups are observed in the spectra of the studied compounds in the region 750-550 cm⁻¹. These bands can be easily identified in the experimental spectra because of their considerable, characteristic shift toward higher wavenumbers in the spectra taken in the N₂ matrices (with respect to their positions in the Ar matrix spectra). Such a characteristic shift was previously observed for several heterocyclic compounds [19,21]. For 6azathiouracils the bands due to the γ N3H vibrations are in all cases placed at higher frequencies

| Table The e theore | 4 xperiments stically calc | al wavenumł culated wave | əers (ř), inte enumbers, al | gral intensi osolute inter | ties (I) and a nsities (A th) | assignments to the and potential ener | ϵ normal modes (Q) of the bands observed in Ar and N ₂ matrices compared with tgy distribution (PED) of the adsorption bands of 2,4-dithio-6-azauracil ^{4,b} |
|--|----------------------------------|-----------------------------|--------------------------------|-------------------------------|--|--|---|
| Mode | Experim | ental | | | Calculate | d SCF/6-311G** | |
| | Ar matr | ż | N ₂ matri | × | | | |
| | <i>ψ</i> / cm ⁻¹ | I (rel.) | $\tilde{v}/{cm^{-1}}$ | I (rel.) | $\tilde{\mathfrak{v}}/{cm^{-1}}$ | $A^{\mathrm{th}/}$ (km mol ⁻¹) | PED/% |
| 61 | 3449 3398 | 339 | 3431 | 481 | 3494 | 177 | vN1H (100) |
| $\begin{array}{c} Q2\\ O3\\ O3\end{array}$ | 3391 | 157 | 3371 | 204 | 3437 3057 | 85 4 | v N3H (100) |
| 2 | 1625 | 4 | | | 1000 | t | (54) UCOV |
| | 1609 | L | | | | | |
| | | | 1599 1501 | 4 v | | | |
| Q4 | 1573 | 96 | 1577 | 0 75 | 1662 | 47 | |
|) | 1557 | sh | 1559 | ; 4 9 | | | (c_1) on c_2 |
| | 1550 | 37 | | | | | |
| 62 | 1515 | 1256 | 1526 | 1120 | 1550 | 1236 | β NH out-of-ph (69) |
| | 1489 | 38 | 150/ 1492 | 6 21 | | | |
| $\mathcal{Q}6$ | 1395 | 56 | 1410 | 4 | 1449 | 99 | BNH in-ph (72) vC5N6 (10) |
| | | | 1404 | sh | | | |
| | 1358 | sh | 1375 | 6 | | | |
| 27 | 1354 | 134 | 1364 | 107 | 1370 | 119 | vNIC2 (25), vC2N3 (14), vC4C5 (14) |
| 08 | 1330 | 06 | 1343 | % | | | |
| à | 1323 | 5 | 1337 1324 | 4" | 1339 | 18 | βC5H (59), vC2N3 (14) |
| $\delta \partial$ | 1273 | 202 | 1274 | 233 | 1263 | 323 | wN3C4 (43) wC4C5 (13) wN1C3 (11) wC3N13 (10) |
| Q^{10} | 1239 | 54 | 1239 | 99 | 1221 | 77 | βR1 (35), vC4S (18), βC5H (14), vC2N3 (12), vC2S (12) |
| | 1221 | 0 | | | | | $[\beta R1 (35), \nu CS in-ph (30), \beta CSH (14), \nu C2N3 (12)]^{6}$ |
| | 1219 | 13 | | | | | |
| | 1206 | 20 | | | | | |
| Ø11 | 1113 1099 | 665 sh | 1117 | 650 | 1098 | 773 | vN6N1 (21), vN1C2 (18), vC4S (15), BNH out-of-ph (14), vC4C5 (13) |
| | | | | | | | [vN6N1 (21), vN1C2 (18), vCS out-of-ph (15), β NH out-of-ph (14), vCACS (13) |
| Q12 | 1049 1010 | 23 4 | 1053 1003 | 17 10 | 1055 | 156 | vN6N1 (47), vC2S (14) [vN6N1 (47), vCS out-of-ph (13)] ^c |

656

| Q13 | 985 | 6 | | | 980 | 7 | <i>β</i> R 1 (44), <i>v</i> C2N3 (16), <i>v</i> NiC2 (12) |
|----------------------|---|--------------|--------------|---------------|-------------------|--|--|
| Q14 015 | 887 | 9 | | | 910 879 | 7 27 | vC5H (109) vC2S (23), vC4S (15), <i>β</i> R2 (13), <i>β</i> R3 (13), vN3C4 (12), vC4C5 (10) |
| 2 | 2 | , | | | | | [vCS out-of-ph (38), <i>β</i> R2 (13), <i>β</i> R3 (13), vN3C4 (12), vC4C5 (10)] ^c |
| | $\left[\begin{array}{c} 726\\ 721 \end{array} \right]$ | | | | | | |
| Q^{16} | 715 | | 766 | 10 | | | |
| | 712 | 105 | 747 | 86 | 729 | 123 | 7, N3H (110) |
| | | - | | | | | [7N3H (110), 7CS In-ph (10)] |
| 017 | 69/ 204 | sh A1 | 707 | 24 | 607 | 17 | r R1 (74) - C4S (71) - C2S (12) |
| ð | 094 | 1 | 10 | ţ | 720 | 17 | $[\tau R]$ (74) 2CS in-ph (32) |
| 018 | 661 | 34 | 663 | 31 | 646 | 20 | R3 (36). VC4C5 (25). R2 (11) |
| د <u>1</u> 0 | 100 | ţ | 600 | , , | 2 |) I | $[\beta R3 (36), \nu C4C5 (25), \nu CS in-ph (12), \beta R2 (11)]^{c}$ |
| | 614 | 32 | | | | | |
| 019 | 604 | 36 | 645 | 43 | 620 | 78 | 7N1H (98), 7C4S (17) |
| : k | | | | | | | [7.N1H (98), 7.CS in-ph (16)] ^c |
| 020 | | | | 609 | 0.004 | | γC2S (56), τR2 (25), γC4S (23) |
| , | | | | | | | [γ CS out-of-ph (76), τ R2 (25)] ^c |
| 021 | 472 | 37 | 473 | 42 | 459 | 52 | β R2 (37), vC2S (24), β R3 (20) |
| 4 | | | | | | | $[\beta R2 (37), \nu CS \text{ out-of-ph} (27), \beta R3 (20)]^c$ |
| Q22 | 440 | 20 | 441 | 16 | 429 | 13 | vC4S (21), <i>β</i> R2 (20), <i>β</i> R3 (16), vC2S (15) |
| , | | | | | | | [νCS in-ph (36), βR2 (20), βR3 (16)] ^c |
| 023 | | | | | 395 | -1 | τ R3 (39), γ C4S (37), τ R2 (15) |
| ł | | | | | | | [τR3 (39), 7CS in-ph (22), 7CS out-of-ph (15), τR2 (15)] ^c |
| 024 | | | | | 372 | 0.2 | β CS in-ph (87) |
| \tilde{o}_{25} | | | | | 209 | 7 | β CS out-of-ph (83) |
| \tilde{o}_{26} | | | | | 142 | 0.01 | π R2 (76), π R1 (13), π R3 (11) |
| 027 | | | | | 116 | ŝ | rR3 (60), r R1 (33) |
| 4 | | | | | | | $[\tau R3 (60), \tau R1 (33), \gamma CS in-ph (12)]^c$ |
| ^a Theoret | ical position | s of absorpt | ion bands v | vere scaled b | by the factor 0.9 | PREs lower | than 10% not included. |
| ^b Abbrev | iations: I, int | h coloriated | bances of ab | sorption ban | ds normalized if | ו such a way נו אישר אישר אישר אישר אישר אישר אישר אישר | hat the observed intensity sum of an inforce is equal to the carviary inverses |

² ADDREVIATIONS: I, megral absorbances of absorption barries for matter in such a way that the base sum of all modes; A^{th} , calculated intensities; rel., relative; sh, shoulder; v, β , τ , γ are defined in Tat ^e For 2,4-dithio-6-azauracil altered definitions of the modes 10, 11, 17, 18, 25 and 26 were applied:

$$\begin{split} S_{10}' &= (2^{-1/2})(S_{10} + S_{11}) \quad vCS \text{ in-ph (in-phase)} \\ S_{11}' &= (2^{-1/2})(S_{10} - S_{11}) \quad vCS \text{ out-of-ph (out-of-phase)} \\ S_{17}' &= (2^{-1/2})(S_{17} + S_{18}) \quad \beta CS \text{ out-of-ph (out-of-phase)} \\ S_{18}' &= (2^{-1/2})(S_{17} - S_{18}) \quad \beta CS \text{ out-of-ph (out-of-phase)} \\ S_{25}' &= (2^{-1/2})(S_{25} + S_{26}) \quad \gamma CS \text{ in-ph (in-phase)} \\ S_{26}' &= (2^{-1/2})(S_{25} - S_{26}) \quad \gamma CS \text{ out-of-ph (out-of-phase)} \\ S_{26}' &= (2^{-1/2})(S_{25} - S_{26}) \quad \gamma CS \text{ out-of-ph (out-of-phase)} \\ \text{with other internal coordinates as in Table 1. PEDs obtained using these coordinates are given in square brackets. \end{split}$$

 $(695 \text{ cm}^{-1}, 688 \text{ cm}^{-1}, 715-712 \text{ cm}^{-1} \text{ (Ar) for})$ 2T6AU, 4T6AU and 24DT6AU, respectively) than the bands due to the γ N1H vibrations (611 cm^{-1} , 566 cm^{-1} , 614–604 cm^{-1} (Ar), for the three azauracils, respectively). This is in agreement with the assignment of the spectra of thiouracils by Graindourze et al. [18]. The effect may be explained by the interactions of the NH groups with the neighbouring C=O and C=S groups. Owing to this interaction the bands due to wagging vibrations of the N3H group (placed between two C=O or C=S groups) are more shifted toward higher frequencies than the bands due to the wagging vibrations of the N1H group, which interacts with only one of the C=O and C=S groups. According to the theoretical calculations the γ CS vibrations are involved to some degree in the normal modes with the main contributions from *γ*N1H.

In the spectra of 2T6AU and 4T6AU, the bands due to the γ CO vibrations are observed at nearly the same frequencies, i.e. at 745 cm⁻¹ and 746 cm⁻¹ (Ar), respectively. The τ R1 and γ NH vibrations are also involved in the normal modes corresponding to these vibrations in both cases.

At low frequencies $(475-430 \text{ cm}^{-1})$ one observes bands due to ν C=S vibrations coupled with ring in-plane deformations. In the spectra of 2T6AU and 4T6AU such bands were found at 452 and 435 cm⁻¹ (Ar). For 24DT6AU, the out-of-phase stretching vibration of the C2=S and C4=S groups contributes to the experimental band at 472 cm⁻¹, whereas the in-phase vibration of these groups contributes to the normal mode with the experimental frequency of 440 cm⁻¹ (Ar).

5. Conclusions

2-Thio-6-azauracil and 4-thio-6-azauracil exist in low-temperature matrices exclusively in their oxothione forms and 2,4-dithio-6-azauracil exists exclusively in the dithione form. The IR spectra of these compounds are well predicted by the theoretical calculations carried out at the SCF/6-311G** level. This has allowed for reasonably reliable assignment of the spectral lines. Many common features were found between the spectra of 2-thio, 4-thio, and 2,4-dithio-6-azauracils and the spectra of 2-thio-, 4-thio-, and 2,4-dithiouracils.

Acknowledgements

This study has been supported by European Union grant no. CIPA-CT 93-0108 and in part by the office of Health and Environmental Research, Department of Energy under contract no. DEFG0393ER61605. One of us (L.A.) acknowledges support for his stay at Université Paul Sabatier by CNRS of France. L.A. would also like to thank Professors J.-P. Daudey and J.-P. Malrieu for their hospitality.

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