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Unimolecular proton-transfer photoreactions in 2,4-dithiouracil and 6-aza-2,4-dithiouracil: A matrix isolation study

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Abstract

Unimolecular proton-transfer photoreactions were studied for 2,4-dithiouracil and 6-aza-2,4-dithiouracil isolated in low-temperature Ar matrices. The IR spectra have revealed that before UV irradiation the matrix-isolated dithiouracils adopted exclusively the dithione tautomeric forms. UV ($\lambda > 320$ nm) irradiation of the matrices led to transfer of protons from N(1)-H or N(3)-H groups to the sulfur atoms of the C(2) = S and C(4) = S thiocarbonyl moieties. The ultimate products of these photoreactions were dithiol tautomeric forms of the studied dithiouracils. For 6-aza-2,4-dithiouracil, photogeneration of a second species was clearly observed. This photoproduct was identified as the thiol–thione tautomer of 6-aza-2,4-dithiouracil. During UV irradiation, the population of this form first grew but then decreased, whereas the population of the dithiol tautomer was increasing monotonically. For 2,4-dithiouracil, the phototautomeric transformations are strongly dominated by the generation of the dithiol product. The second product, the thiol–thione form of 2,4-dithiouracil, was photogenerated only in trace amounts. The products of the investigated photoreactions were identified by comparison of their IR spectra with the spectra calculated at the DFT(B3LYP)/6-311++G(2d,p) level.

Keywords: 2,4-Dithiouracil; 6-Aza-2,4-dithiouracil; Matrix isolation; IR spectra; Phototautomerism; Proton-transfer

1. Introduction

Photochemical, intramolecular single-proton-transfer processes were previously observed in our laboratory for simple thioamides (such as thioacetamide [1] and thiourea [2], Scheme 1) as well as for heterocyclic thione compounds (such as 2(*1H*)-pyridinethione [3] and 4(*3H*)-pyrimidinethione [4], Scheme 2). Upon UV irradiation of monomers of these compounds isolated in low-temperature inert gas matrices, a proton from the N–H group was shifted to the C=S group placed in the α-position. That led to the conversion of the thione form of studied compounds into the thiol tautomer. On this way, photochemical generation and spectral characterization of the (till that time never observed) thiol forms of simple thioamides (thioacetamide and thiourea) was possible. Very recently, analogous unimolecular thione → thiol phototautomeric transformations were found to occur also for matrix-isolated monomers of 4-thiouracil [5] (see Scheme 3) and 2-thiouracil [6] (see Scheme 4). For these species, the photoprocesses involving transfer of protons from the N–H groups to the thiocarbonyl (C=S) groups dominated strongly over the transfer of protons to the carbonyl (C=O) groups. Putative phototautomerization in S_2 excited state, revealed by fluorescence picosecond laser spectroscopy, was also reported [7] for 4-thiouridine in acetonitrile solution.

For 2,4-dithiouracil (24dtU), the presence of two N–H and two C=S groups in a molecule opens the gate for more than one, simple pathway of the UV-induced thione → thiol phototautomeric reaction. The thiol–thione tautomers of the compound could be expected as products of a single-proton-transfer photoreaction and the dithiol tautomer can be photogenerated in a double-proton-transfer process. In our previous study on the unimolecular photochemical changes of 24dtU isolated in argon matrices [8], the dithiol tautomer of 24dtU, generated by the transfer of both N–H protons to the thiocarbonyl C=S groups, was detected as the only photoproduct (Scheme 5). This was the first observation of an intramolecular double-proton-transfer photoprocess. Afterwards, a UV-induced transfer of

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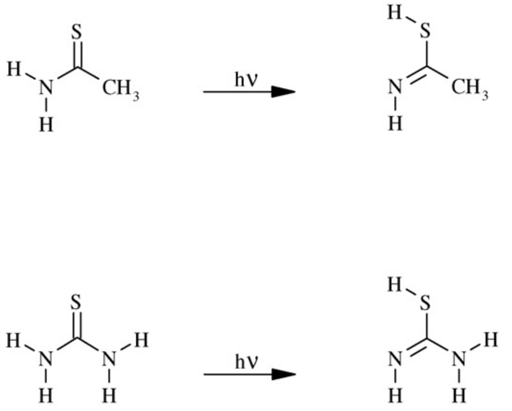
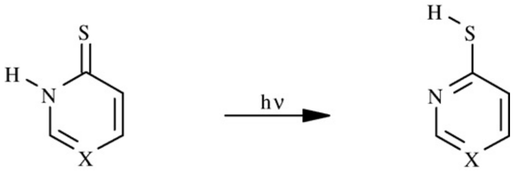
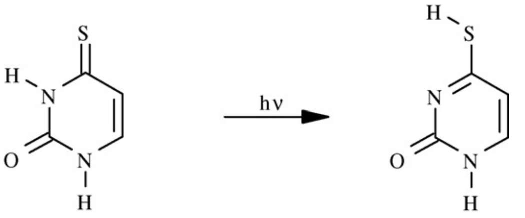


Scheme 1.



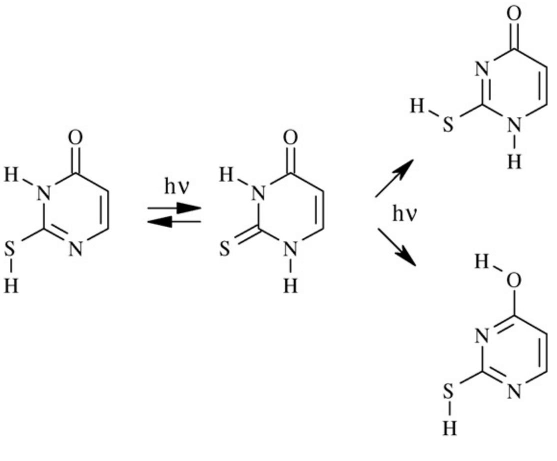
X = CH or N

Scheme 2.

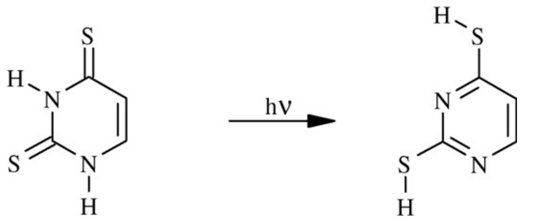


Scheme 3.

two protons was observed also for other compounds (such as dithiooxamide [9] and 2,6-dithiopurine [10]). Finally, a photoinduced trithione → trithiol unimolecular transfer of three protons was found for trithiocyanuric acid [11].



Scheme 4.



I II

Scheme 5.

In the present work UV-induced processes in monomeric 6-aza-2,4-dithiouracil (6a24dtU) were investigated. One could expect that the unimolecular photochemistry of 6a24dtU should be quite similar to that of 24dtU. And indeed, there are similarities between the photochemical behavior of the two compounds, but there are also clear points of difference. The observations of the pathways of photochemical proton-transfer reactions in 6a24dtU prompted us to have a new, very detailed look at the unimolecular phototransformations of 24dtU.

2. Experimental

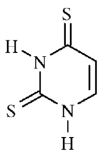
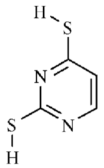
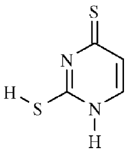
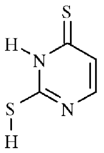
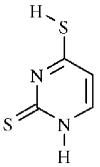
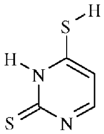
2,4-Dithiouracil used in the present study was a commercial product supplied by Aldrich. The sample of 6-aza-2,4-dithiouracil was synthesized using the procedure described in Ref. [12]. To prepare a low-temperature matrix, solid sample of a studied compound was electrically heated in a miniature glass oven placed in the vacuum chamber of a continuous-flow helium cryostat. The vapors of the compound were deposited, together with a large excess of inert gas (argon), on a CsI window cooled to 10 K. The argon matrix gas of spectral purity 6.0 was supplied by Linde AG. The IR spectra were recorded with 0.5 cm^{-1} resolution using the Thermo Nicolet Nexus 670 FTIR spectrometer equipped with a KBr beam splitter and a DTGS detector. The intensities of the IR absorption bands were measured by numerical integration. Matrices were irradiated with light from HBO200 high-pressure mercury lamp fitted with a water filter and a WG320 cutoff filter transmitting light with $\lambda > 320$ nm.

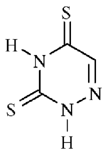
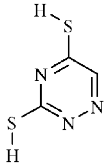
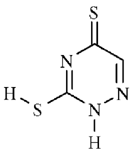
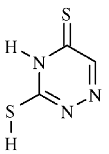
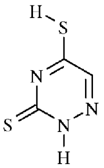
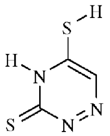
3. Computational details

The geometries of the isomeric forms of 24dtU and 6a24dtU were optimized using the hybrid Hartree-Fock and density functional theory DFT(B3LYP) method [13–15] as well as at the second-order perturbation theory MP2 level [16]. At the fully optimized equilibrium geometries the relative energies of the isomeric forms of 24dtU and 6a24dtU were calculated using both theoretical approaches (Table 1).

The DFT(B3LYP) harmonic vibrational frequencies and IR intensities were calculated at geometries optimized at this level. All quantum-mechanical calculations were performed with the GAUSSIAN 98 program [17] using the 6-311++G(2d,p) basis set. To correct for the systematic shortcomings of the applied methodology (mainly for anharmonicity), the predicted vibrational wavenumbers were scaled down by a single factor of 0.98.

Table 1
Relative electronic (ΔE_{el}), zero-point vibrational (ΔZPE) and total ($\Delta E_{total} = \Delta E_{el} + \Delta$ZPE) energies of tautomeric forms of 2,4-dithiouracil and 6-aza-2,4-dithiouracil

	 **I**	 **II**	 **III**	 **IV**	 **V**	 **VI**
ΔE_{el}(DFT)	0	44.9	83.7	42.3	54.6	79.3
ΔE_{el}(MP2)	0	31.8	79.3	37.3	52.8	76.7
ΔZPE(DFT)	0	−20.4	−12.5	−10.6	−11.1	−12.4
ΔE_{total}[a]	0	11.4	66.8	26.7	41.7	64.3

	 **6aI**	 **6aII**	 **6aIII**	 **6aIV**	 **6aV**	 **6aVI**
ΔE_{el}(DFT)	0	74.6	70.4	71.1	56.2	124.2
ΔE_{el}(MP2)	0	60.1	67.1	64.6	53.6	121.8
ΔZPE(DFT)	0	−21.6	−11.8	−12.1	−10.8	−14.1
ΔE_{total}[a]	0	38.5	55.3	52.5	42.8	107.7

The energies of the dithione forms **I** and **6aI** were taken as references. The calculations were carried out using the 6-311++G(2d,p) basis set.

[a] ΔE_{total} obtained using MP2 values of ΔE_{el} and DFT(B3LYP) values of ΔZPE. Electronic energies obtained for the most stable dithione forms **I** and **6aI** are: 2,4-dithiouracil: E_{el}(DFT) = −1060.8665 a.u., E_{el}(MP2) = −1059.0797 a.u.; 6-aza-2,4-dithiouracil: E_{el}(DFT) = −1076.8810 a.u., E_{el}(MP2) = −1075.0820 a.u.

In order to enable the potential energy distribution (PED) analysis of the normal modes [18,19], the calculated force constants with respect to Cartesian coordinates were transformed to the molecule-fixed internal coordinates. The list of the used internal coordinates is given in Table 2. The elements of the PED matrices, calculated for thiol–thione and dithione tautomers of 6a24dtU are presented in Tables 3 and 4.

4. Results and discussion

2,4-Dithiouracil as well as 6-aza-2,4-dithiouracil can adopt six tautomeric forms with canonical structures (see Table 1). The relative energies of the tautomeric forms of 24dtU and 6a24dtU were theoretically predicted, within the present study, at the MP2/6-311++G(2d,p) level. According to these calculations (summarized in Table 1), the dithione tautomers should be the most stable forms of both 24dtU and 6a24dtU, whereas the energies of the thiol–thione and dithiol tautomers should be significantly higher. These predictions are in full agreement with the previous reports on tautomerism of monomeric 24dtU [20–23] and 6a24dtU [12].

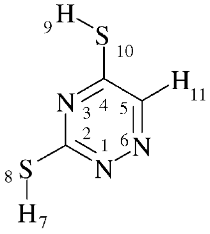
Moreover, the rotations of the SH group(s) in thiol–thione and dithiol tautomers can give rise to seven additional isomeric structures of dithiouracils (see Ref. [21]). In comparison to the forms reported in Table 1, the structures resulting from rotation of one or two SH group(s) are destabilized by the lack of attractive interaction with the lone electron pair(s) of neighboring nitrogen atom(s) and/or by repulsion between two hydrogen atoms placed in direct vicinity. The set of all possible 13 structures of 24dtU has been considered in the theoretical work of Lamsabhi et al. [21]. Due to destabilizing effects described above, the energies (predicted at the MP2 level [21]) of rotamers not included in Table 1 were systematically higher than their counterparts **I–VI**.

In the gas phase and in low-temperature Ar and N_2 matrices, molecules of 24dtU and 6a24dtU were found only in the dithione tautomeric forms **I** and **6aI**, respectively. The dithione tautomer was also determined as the only form of 24dtU adopted in the crystalline phase of the compound [24].

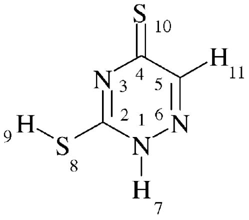
It is also interesting to compare the relative energies of the tautomers (**6aII**, **6aIV** and **6aVI**) of 6a24dtU (with respect to the dithione form **6aI**) with the relative energies of the corresponding forms of 24dtU. One sees (Table 1) that in 6a24dtU the presence (in the heterocyclic ring) of two neighboring nitrogen atoms without attached hydrogens substantially increases the energy of the system. The reason for that is the repulsion of the overlapping lone-electron pairs of both nitrogen atoms.

The IR spectrum of 6a24dtU isolated in a low-temperature argon matrix, recorded in the current work, is the same as that reported in the previous paper [12]. Irradiation of 6a24dtU monomers with UV (λ > 320 nm) light induced photochemical transformations, which were detected by means of the IR spectra collected at consecutive stages of the photoprocess (Fig. 1). The bands decreasing systematically during the UV irradiation belong to the spectrum of the initially trapped substrate of the phototransformations. The experimental spectrum consisting of these bands is well reproduced by the theoretical spectrum calcu-

Table 2
Internal coordinates used in the normal mode analysis for the dithiol tautomer **6aII** and the thiol–thione tautomer **6aIII** of 6-aza-2,4-dithiouracil



6aII



6aIII

$S_1 = r_{1,2}$		νN1C2
$S_2 = r_{2,3}$		νC2N3
$S_3 = r_{3,4}$		νN3C4
$S_4 = r_{4,5}$		νC4C5
$S_5 = r_{5,6}$		νC5C6
$S_6 = r_{6,1}$		νNN
$S'_7 = r_{1,7}$	**6aIII**	νN1H
$S''_7 = r_{8,7}$	**6aII**	νS8H
$S_8 = r_{2,8}$		νC2S
$S'_9 = r_{8,9}$	**6aIII**	νS8H
$S''_9 = r_{9,10}$	**6aII**	νS10H
$S_{10} = r_{4,10}$		νC4S
$S_{11} = r_{5,11}$		νC5H
$S_{12} = (6^{-1/2})(\beta_{2,6,1} - \beta_{1,3,2} + \beta_{2,4,3} - \beta_{3,5,4} + \beta_{4,6,5} - \beta_{5,1,6})$		βR1
$S_{13} = (12^{-1/2})(2\beta_{2,1,6} - \beta_{1,3,2} - \beta_{2,4,3} + 2\beta_{3,5,4} - \beta_{4,6,5} - \beta_{5,1,6})$		βR2
$S_{14} = (1/2)(\beta_{1,3,2} - \beta_{2,4,3} + \beta_{4,6,5} - \beta_{5,1,6})$		βR3
$S'_{15} = (2^{-1/2})(\beta_{7,6,1} - \beta_{7,2,1})$	**6aIII**	βN1H
$S''_{15} = \beta_{7,2,8}$	**6aII**	βS8H
$S'_{16} = \beta_{9,2,8}$	**6aIII**	βS8H
$S'_{16} = \beta_{9,4,10}$	**6aII**	βS10H
$S_{17} = (2^{-1/2})(\beta_{8,1,2} - \beta_{8,3,2})$		βC2S
$S_{18} = (2^{-1/2})(\beta_{10,3,4} - \beta_{10,5,4})$		βC4S
$S_{19} = (2^{-1/2})(\beta_{11,4,5} - \beta_{11,6,5})$		βC5H
$S_{20} = (6^{-1/2})(\tau_{1,2,3,4} - \tau_{2,3,4,5} + \tau_{3,4,5,6} - \tau_{4,5,6,1} + \tau_{5,6,1,2} - \tau_{6,1,2,3})$		τR1
$S_{21} = (1/2)(\tau_{1,2,3,4} - \tau_{3,4,5,6} + \tau_{4,5,6,1} - \tau_{6,1,2,3})$		τR2
$S_{22} = (12^{-1/2})(-\tau_{1,2,3,4} + 2\tau_{2,3,4,5} - \tau_{3,4,5,6} - \tau_{4,5,6,1} + 2\tau_{5,6,1,2} - \tau_{6,1,2,3})$		τR3
$S'_{23} = \gamma_{7,6,1,2}$	**6aIII**	γN1H
$S''_{23}(2^{-1/2})(\tau_{7,8,2,1} + \tau_{7,8,2,3})$	**6aII**	τS8H
$S'_{24} = (2^{-1/2})(\tau_{9,8,2,3} + \tau_{9,8,2,1})$	**6aIII**	τS8H
$S''_{24} = (2^{-1/2})(\tau_{9,10,4,3} + \tau_{9,10,4,5})$	**6aII**	τS10H
$S_{25} = \gamma_{8,1,2,3}$		γC2S
$S_{26} = \gamma_{10,3,4,5}$		γC4S
$S_{27} = \gamma_{11,4,5,6}$		γC5H

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

lated at the DFT(B3LYP)/6-311++G(2d,p) level, for the dithione tautomer **6aI** (see Fig. 2). This confirms the assignment of the dithione structure **6aI** to the only form of 6a24dtU observed in the matrix before any irradiation.

Decrease of the bands due to the substrate of the photoreaction (form **6aI**) was accompanied by appearance of new bands indicating generation of photoproduct(s). As it can be seen in Fig. 1, the new bands did not uniformly change their intensities during the photoprocess. By monitoring the intensity changes at consecutive stages of the UV-induced reaction, it was possible to determine two groups of bands due to photoproduced species. Bands belonging to one of the sets appeared and were increasing monotonically during the UV-induced process, whereas the other set of bands first appeared and increased in intensity, but after prolonged irradiation began to decrease. These observations lead to a conclusion that two photoproducts were generated upon exposure of matrix-isolated 6a24dtU to UV light. Having recorded the IR spectra at different stages of the photoprocess, it was possible (by electronic subtractions of the spectra multiplied by appropriate scaling factors) to separate the spectra of the two photoproduced species.

For the photoproduct first being generated, but then consumed during the photoprocess, one band due to νNH vibration (at 3452 cm^{-1}) and one band due to νSH vibration (at 2598 cm^{-1}) were observed in the experimental IR spectrum (Fig. 3). This suggests a thiol–thione structure of this photoproduced species. The experimental spectrum of this photoproduct was compared with the spectra of different thiol–thione tautomers of 6a24dtU

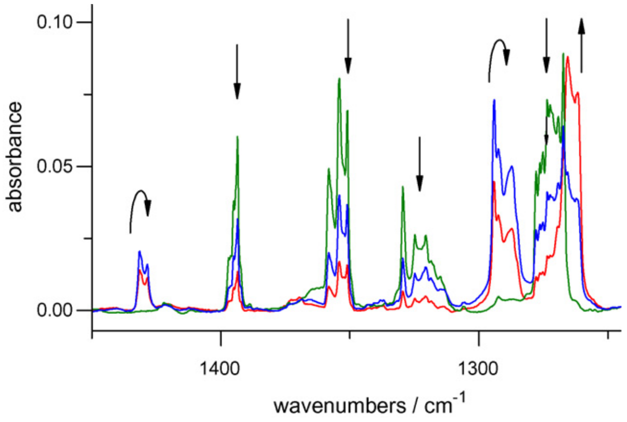


Fig. 1. Portion of the IR spectrum of 6-aza-2,4-dithiouracil isolated in an Ar matrix: (green line) after deposition of the matrix; (blue line) after 1 h of UV ($\lambda > 320$ nm) irradiation; (red line) after subsequent 3 h of UV ($\lambda > 320$ nm) irradiation. Arrows indicate the direction of changes of the band intensities with the time of irradiation.

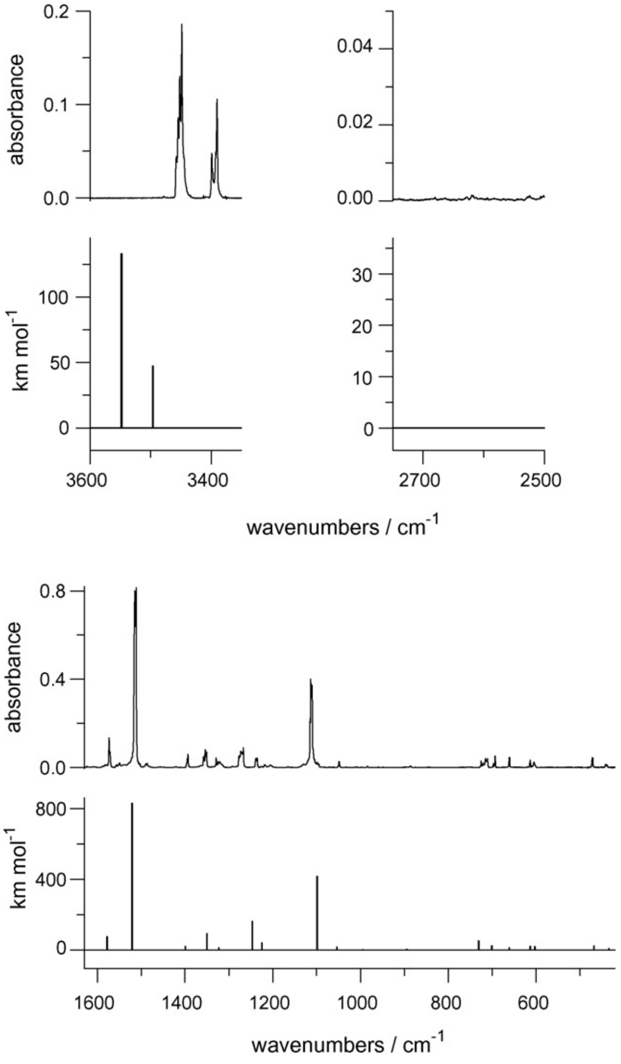


Fig. 2. The comparison of the experimental spectrum of 6-aza-2,4-dithiouracil isolated in an Ar matrix with the spectrum of tautomer **6aI** theoretically simulated at the DFT(B3LYP)/6-311++G(2d,p) level. The calculated wavenumbers were scaled by the single factor of 0.98.

calculated at the DFT(B3LYP)/6-311++G(2d,p) level. Satisfactory agreement with the experimental spectrum was achieved only in the case of the spectrum predicted for tautomer **6aIII** (Fig. 3).

Table 3
Experimental wavenumbers ($\tilde{\nu}$, cm^{-1}) and relative integral intensities (I) of the absorption bands in the spectrum of the photoproduct generated and then consumed upon UV irradiation of 6-aza-2,4-dithiouracil isolated in an Ar matrix, compared with wavenumbers ($\tilde{\nu}$, cm^{-1}), absolute intensities (A^{th}, km mol^{-1}) and potential energy distribution (PED, %) calculated for the thiol–thione form **6aIII**

Experimental Ar matrix		Calculated B3LYP/6-311++G(2d,p)		
$\tilde{\nu}$	I^{a}	$\tilde{\nu}^{\text{b}}$	A^{th}	PED$^{\text{c}}$ (%)
3459, **3452**	166	3449	144	νN1H (100)
		3138	0.1	νC5H (100)
2607, 2602, **2598**	18	2634	11	νS8H (100)
1580	56	1592	64	νC5N6 (63), βN1H (18)
1526, 1523	318	1527	588	νC2N3 (54), βN1H (30)
1432, 1429	41	1425	64	βN1H (32), νN1C2 (23), νC2N3 (21), νC5N6 (11)
1338	17	1335	23	βC5H (60), νC5N6 (10)
1294, 1287	418	1276	355	νN3C4 (44), βN1H (12), νN1C2 (12)
1231, 1227	52	1215	83	βR1 (41), νC4S (23)
1150, 1146	171	1132	119	νC4C5 (38), νN1C2 (23)
1039, **1035**	35	1046	28	νNN (69)
996, **992**	54	983	46	βR1 (43), νN1C2 (12), νN3C4 (20)
933	3	932	4	γC5H (107)
900	19	886	27	βS8H (70)
		848	21	βR2 (17), νC2S (16), βS8H (14), νN3C4 (14), βR3 (13), νC4S (12)
715	5	729	4	τR1 (78), γC4S (20), γC2S (12)
660	8	657	7	βR3 (44), νC4C5 (23)
		608	0.3	γC2S (48), γC4S (30), τR2 (27)
538, **531**	40	504	67	γN1H (77), γC2S (12), τR3 (11)
		466	13	βR2 (53), νC4S (20), νC2S (11)
		400	2	νC2S (42), βR3 (23), νC4S (10)
		391	0.4	τR3 (36), γN1H (25), γC4S (23), τR1 (11)
		358	3	βC4S (47), βC2S (32)
		235	36	τS8H (93)
		199	2	βC2S (54), βC4S (32)
		150	0.02	τR2 (34), γC2S (28), τR1 (25), γC4S (11)
		58	0.2	τR3 (55), τR2 (41)

Wavenumbers of the strongest components of split bands are bold.

[a] Relative integrated intensities.

[b] Theoretical positions of absorption bands were scaled down by a factor of 0.98.

[c] PEDs lower than 10% are not included. Definition of internal coordinates is given in Table 2.

Table 4
Experimental wavenumbers ($\tilde{\nu}$, cm^{-1}) and relative integral intensities (I) of the absorption bands in the spectrum of ultimate photoproduct generated upon UV irradiation of 6-aza-2,4-dithiouracil isolated in an Ar matrix, compared with wavenumbers ($\tilde{\nu}$, cm^{-1}), absolute intensities (A^{th}, $\mathrm{km\,mol}^{-1}$) and potential energy distribution (PED, %) calculated for the dithiol form **6aII**

Experimental Ar matrix		Calculated B3LYP/6-311++G(2d,p)		
$\tilde{\nu}$	I[a]	$\tilde{\nu}$[b]	A^{th}	PED[c] (%)
		3120	1	νC5H (100)
2606	4	2621	4	νS10H (100)
2594	4	2617	4	νS8H (100)
1513, **1511**, 1509	179	1507	264	νC5N6 (34), βC5H (22), νC2N3 (13), νN3C4 (10), νC4C5 (10)
1491, **1486**	229	1487	140	νN3C4 (43), νC4C5 (23), νNN (10)
1370	15	1381	10	βC5H (41), νC2N3 (23), νN1C2 (11), νNN (11)
1266, 1262	315	1264	294	νC2N3 (30), νC5N6 (23), βR1 (13), νN1C2 (12)
1210, 1204, **1196**	66	1189	52	βR1 (28), νN3C4 (17), ν C5N6 (16), νC4S (12), νC4C5 (11)
1143, **1140**	110	1146	100	νN1C2 (22), βC5H (20), νC5N6 (20), νC4C5 (16)
1049	60	1059	62	νNN (49), νN1C2 (19), νN3C4 (13)
989, **987**	17	994	3	βR1 (37), νNN (18), νC2N3 (17)
956	4	967	4	βS8H (75)
902	11	889	35	βS10H (76), βS8H (11)
		883	7	γC5H (106)
848, 842	42	840	66	βR2 (31), νC4S (19), νC2S (16), βR3 (16)
818	36			
		782	0.3	τR1 (90), γC2S (15)
667, 662	1	676	2	βR3 (46), βR2 (22), νC4C5 (13)
593	1	601	3	γC2S (45), γC4S (32), τR2 (17)
		445	3	νC2S (36), βR2 (27), νC4S (17), βR2 (13)
		430	7	τR3 (69), γC2S (15)
		395	0.4	νC4S (35), νC2S (25), βR3 (11)
		333	7	βC2S (45), βC4S (42)
		326	12	τS8H (98)
		291	20	τS10H (97)
		182	1	βC4S (45), βC2S (44)
		161	0.4	γC4S (41), γC2S (23), τR3 (21), τR1 (10)
		142	4	τR2 (81), γC4S (15)

Wavenumbers of the strongest components of split bands are bold.

[a] Relative integrated intensities.

[b] Theoretical positions of absorption bands were scaled down by a factor of 0.98.

[c] PEDs lower than 10% are not included. Definition of internal coordinates is given in Table 2.

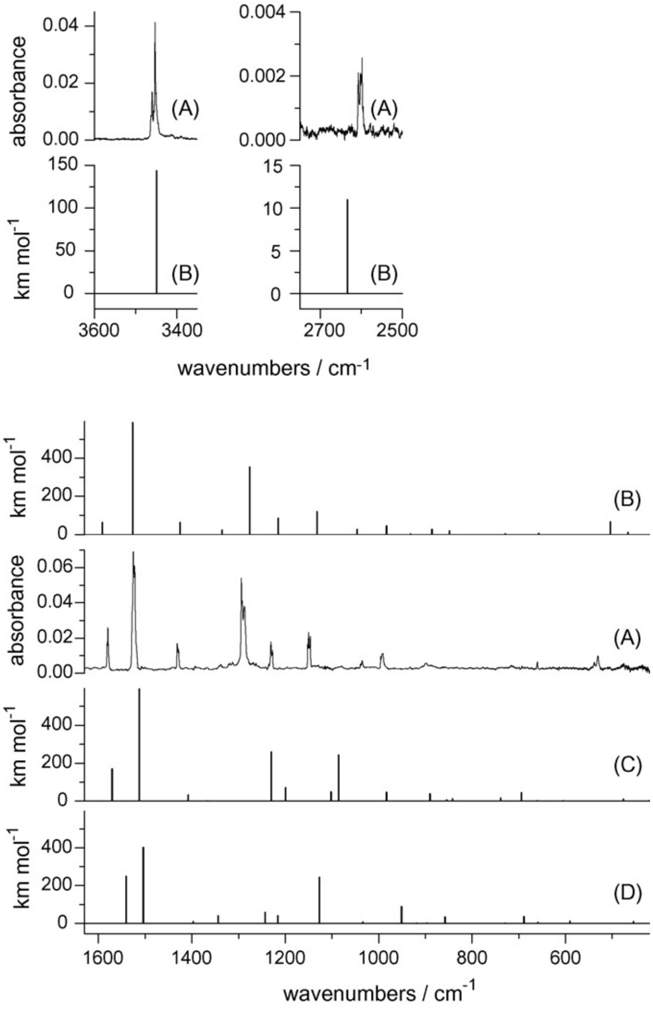


Fig. 3. The comparison of: (A) the experimental spectrum of the photoproduct that first was generated but then consumed during the UV ($\lambda > 320$ nm) irradiation of 6-aza-2,4-dithiouracil isolated in an Ar matrix with the spectra of the thiol–thione tautomers (B) **6aIII**; (C) **6aV**; (D) **6aIV** theoretically simulated at the DFT(B3LYP)/6-311++G(2d,p) level. The calculated wavenumbers were scaled by the single factor of 0.98.

For the photoproduct monotonically growing during the whole period of UV irradiation, the IR bands due to νSH vibrations were found at 2606, 2594 cm^{-1} whereas no bands were observed in the spectral region where the absorptions due to νNH vibrations could be expected (Fig. 4). Hence, the dithiol tautomer **6aII** seemed to be the best candidate for the structure of the ultimate product of the phototransformations of 6a24dtU (Scheme 6). Comparison of the whole mid-IR range of the spectrum of this photoproduct with the spectrum calculated for isomer **6aII** (Fig. 4) confirms the identification of this form as the final product of unimolecular proton-transfer photoreactions in 6a24dtU.

The experimental spectra of both photoproducts are so well reproduced by the results of the theoretical calculations that the structure identification seems to be unequivocal. The assignment of the IR bands observed in the spectra of photoproducts **6aIII** and **6aII** to the normal modes calculated at the DFT(B3LYP)/6-311++G(2d,p) level is given in Tables 3 and 4, respectively.

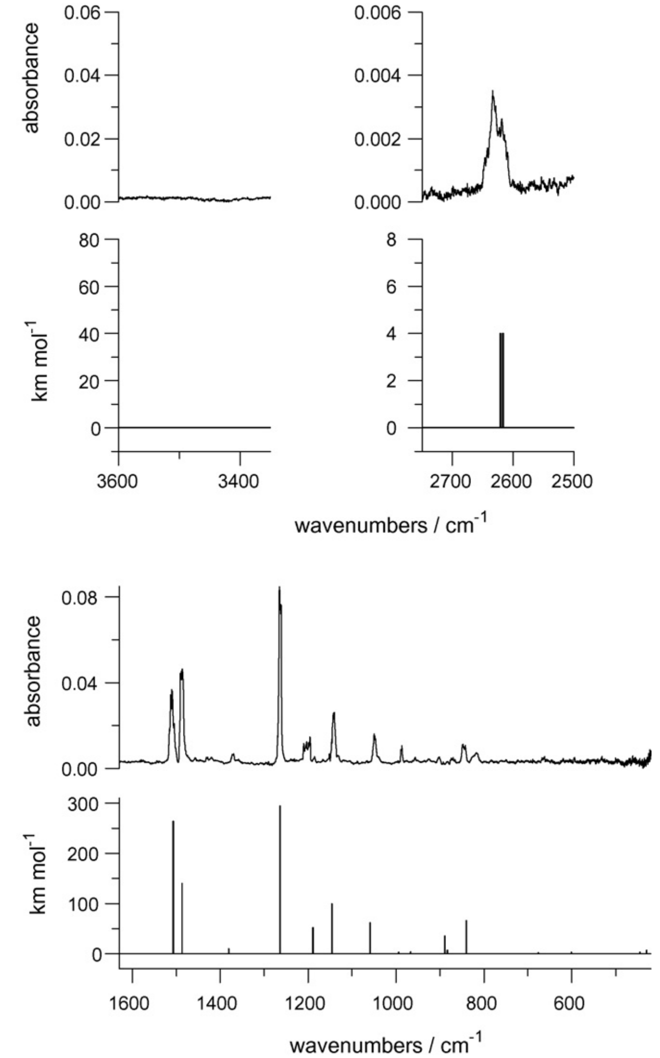
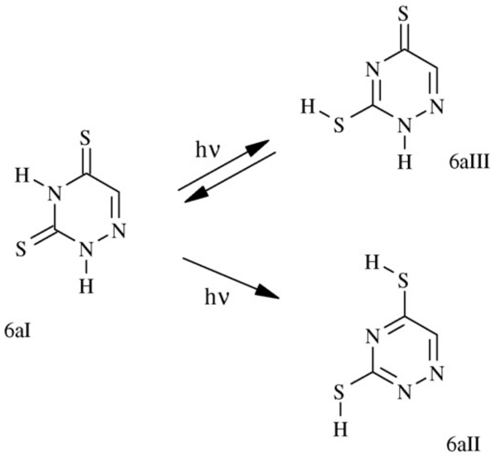


Fig. 4. The comparison of the experimental spectrum of the ultimate photoproduct generated upon the UV ($\lambda > 320$ nm) irradiation of 6-aza-2,4-dithiouracil isolated in an Ar matrix with the spectrum of the dithiol tautomer **6aII** theoretically simulated at the DFT(B3LYP)/6-311++G(2d,p) level. The calculated wavenumbers were scaled by the single factor of 0.98.



Scheme 6.

At the first glance, the progress of the UV-induced phototransformations presented in Fig. 1 might seem to be an indication of production of the dithiol form **6aII** involving intermediacy of a thiol–thione tautomer. If this thiol–thione intermediate was form **6aIII** and the first step of the **6aI** → **6aII** transformation was the **6aI** → **6aIII** single-proton transfer, then the second **6aIII** → **6aII** act would involve a long-distance proton transfer across the whole molecule: from N1 to the remote C4=S thiocarbonyl (see Scheme 6). Hence, it does not seem likely that form **6aIII** is a transient product in the conversion of **6aI** into **6aII**.

Because in the course of the UV-induced transformations of 6a24dtU the population of form **6aIII** first increases but then decreases, there must be a photoprocess that consumes this form. According to the discussion above, it does not seem probable that form **6aIII** is transformed directly to **6aII** that is to the final product of the phototransformations of 6a24dtU. The intermediates, through which goes the transformation of **6aIII** into the ultimate photoproduct **6aII** are not known. In this respect, a process involving a photoinduced reverse thiol → thione proton shift, transforming **6aIII** back into the initial **6aI** form (see Scheme 6) seems to be the most likely.

Numerous examples of UV-induced thione → thiol proton transfers were observed in our previous works [1–6,8,9], but the

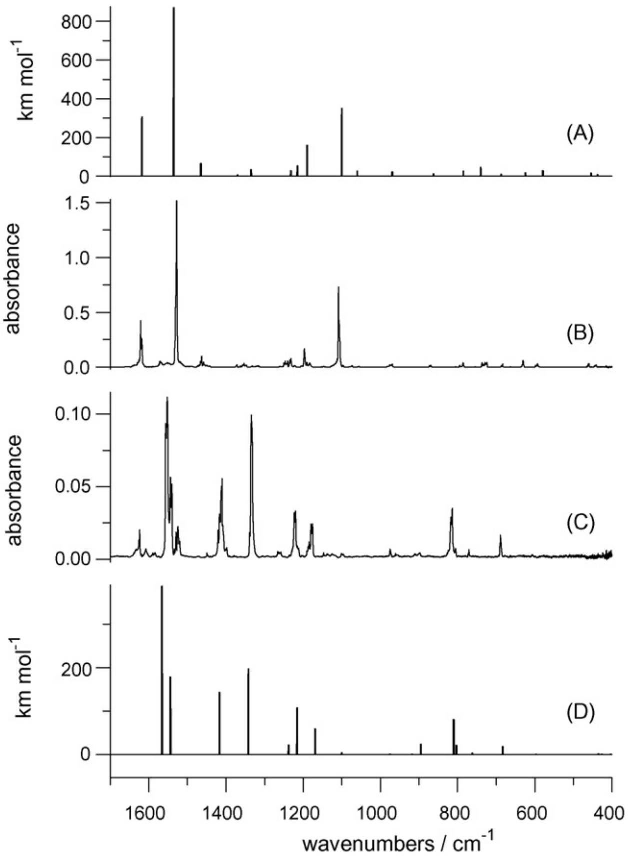


Fig. 5. The comparison of the experimental spectrum of 2,4-dithiouracil isolated in an Ar matrix recorded before (B) and after (C) UV ($\lambda > 320$ nm) irradiation with the theoretical spectra of the dithione tautomer **I** (A) and the dithiol tautomer **III** (D) predicted at the DFT(B3LYP)/6-311++G(2d,p) level. The calculated wavenumbers were scaled by the single factor of 0.98.

experimental evidence of a concomitant photoreaction in the opposite (thiol → thione) direction has been found only very recently, for monomers of 2-thiouracil (Scheme 4), 6-aza-2-thiotymine, 1-methyl-2-thiouracil and 3-methyl-2-thiouracil [6] isolated in low-temperature Ar matrices. It is quite probable that such a thiol → thione back reaction plays a role in UV-induced consumption of photoproduct **6aIII**.

For 24dtU isolated in a low-temperature Ar matrix [8,25], the UV-induced photoreaction converts the initial dithione form **I** into the dithiol tautomer **II** (Scheme 5). The structures of the substrate and the product of this phototransformation were identified on the basis of the very good agreement between the experimental IR spectra of these species and the spectra theoretically predicted for tautomers **I** and **II**, respectively (see Fig. 5, compare also Ref. [8]). Hence, the transformation of the dithione form **I** into the dithiol form **II**, analogous to the **6aI** → **6aII** photoconversion in 6a24dtU, is clearly documented also for 24dtU. In spite of this similarity, it is evident that the analogy between the unimolecular phototransformations in 6a24dtU and in 24dtU is not very tight. The second photoproduct, analogous to form **6aIII** of 6a24dtU, is seemingly missing in case of 24dtU. No other IR bands than those belonging to the initial dithione form **I** or the final dithiol photoproduct **II** were observed in the previous study [8]. In the present work, only upon very careful examination of the spectra recorded at consecutive stages of the progress of the UV-induced processes in matrix-isolated 24dtU, it was possible to identify several very weak IR bands, which appeared and then diminished during the irradiation. These bands are presented in Fig. 6. By analogy with the case of 6a24dtU, appearance of a set of such bands can be tentatively interpreted as an indication of photogeneration of very low quantities of form **III**. However, a positive assignment of structure **III** to the second photoproduct generated upon UV-irradiation of 24dtU is not possible on the basis of observation of just several weak bands, which (by accident) do not overlap with much stronger absorptions of the main photoproduct **II**.

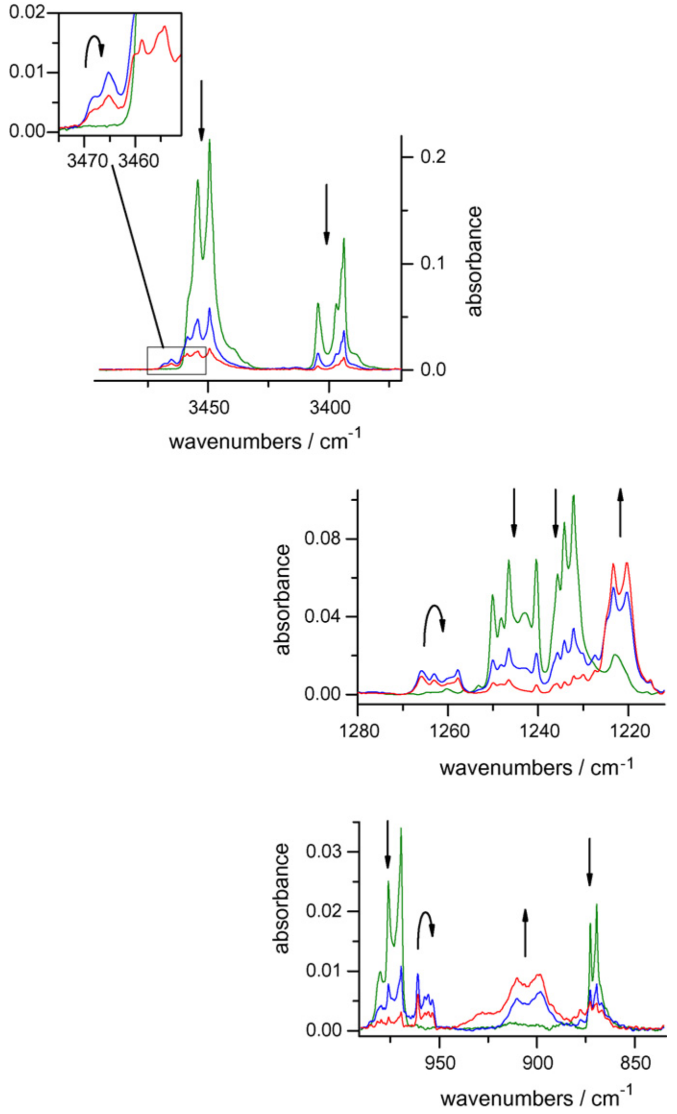


Fig. 6. Fragments of the IR spectrum of 2,4-dithiouracil isolated in an Ar matrix: (green line) after deposition of the matrix; (blue line) after 2 h of irradiation with UV ($\lambda > 320$ nm) light; (red line) after subsequent 2 h of irradiation with UV ($\lambda > 320$ nm) light. Arrows indicate the direction of changes of the band intensities with the time of irradiation.

5. Concluding discussion

Intramolecular proton-transfer photoreactions were observed for 2,4-dithiouracil and 6-aza-2,4-dithiouracil. Thiol–thione and dithione tautomers of these two compounds were generated in these UV-induced processes. For both dithiouracils in question, the final product of the phototransformations was the dithiol tautomer with both labile protons transferred from N–H groups to the thiocarbonyl moieties (Scheme 6).

No experimental evidence was found, which would support either stepwise or concerted mechanism of the transfer of two protons resulting in formation of the dithiol tautomers. The first act of the stepwise mechanism would involve photoinduced transfer of one of the protons and generation of the thiol–thione tautomers **IV** or **V** (**6aIV** or **6aV**). The dithiol tautomer **II** (**6aII**) would be generated in a subsequent act by transfer of the second proton. In principle, such a mechanism is possible, but no spectral indication of the appearance of either **IV** or **V** (**6aIV** or **6aV**) could be found in the IR spectra recorded at different stages of the UV-induced transformations. This does not necessarily mean that these intermediates are not generated at all. If the efficiency of the second act was much higher than that of the transfer of the first proton, the concentrations of the intermediates **IV** or **V** (**6aIV** or **6aV**) would be very low at any stage of the photoprocess.

On the other hand, there are no experimental or theoretical arguments, which would allow ruling out the concerted transfer of two protons in a single act, following excitation of a molecule. Similar dilemmas concerning stepwise or synchronous mechanism of the transfer of two or three protons appear also for other species undergoing photoinduced proton transfer, e.g. 2,6-dithiopurine [10] or trithiocyanuric acid [11]. In none of these cases, intermediate forms with only one proton transferred (or with two protons transferred, for trithiocyanuric acid) were ever observed.

It is worthy to stress that the dithiol and thiol–thione tautomers generated upon UV irradiation of matrix-isolated 6a24dtU and 24dtU have never been observed either in the gas phase or in condensed phases (solutions [26–30] and solids [24]). Because of the high relative energies of these tautomers, their thermal population is very improbable; they could be generated only photochemically. The spectroscopic characterization of such species (using stationary techniques) is possible only due to stabilization of these forms in low-temperature, inert matrices.

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