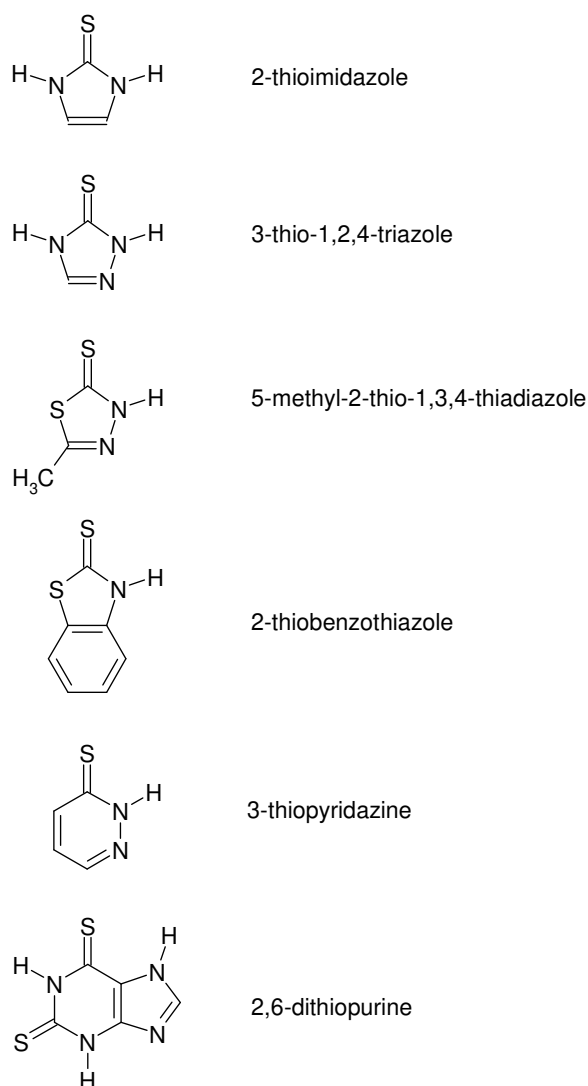# Intramolecular Hydrogen-Atom Tunneling in Matrix-Isolated Heterocyclic Compounds: 2-Thiouracil and Its Analogues

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Supporting Information

Scheme S1. Structures of heterocyclic compounds with five- and six-membered heterocyclic rings for which no spontaneous thiol → thione tautomerization was observed.
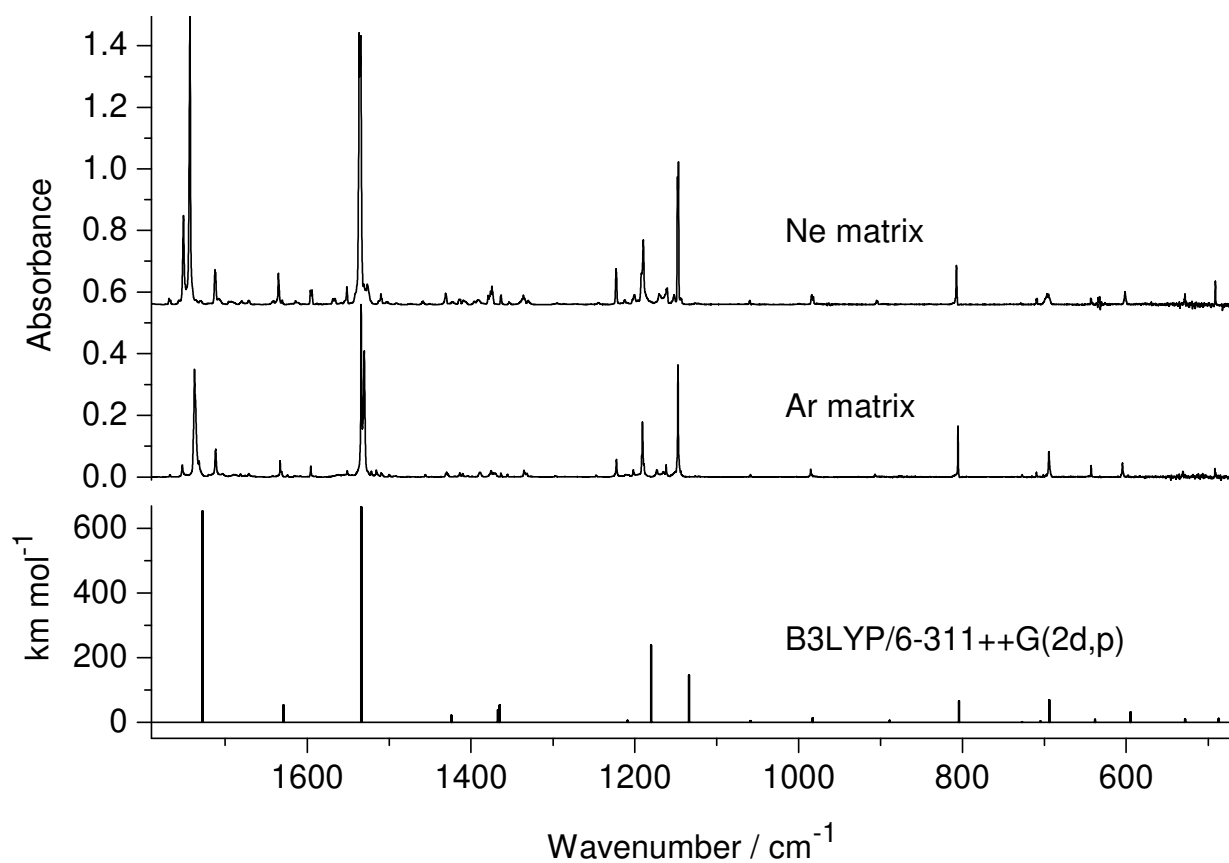
Figure S1. Infrared spectra of 2-thiouracil monomers isolated in Ar and Ne matrices compared with the theoretical spectrum calculated at the B3LYP/6-311++G(2d,p) level for the most stable oxo-thione tautomer **I**.
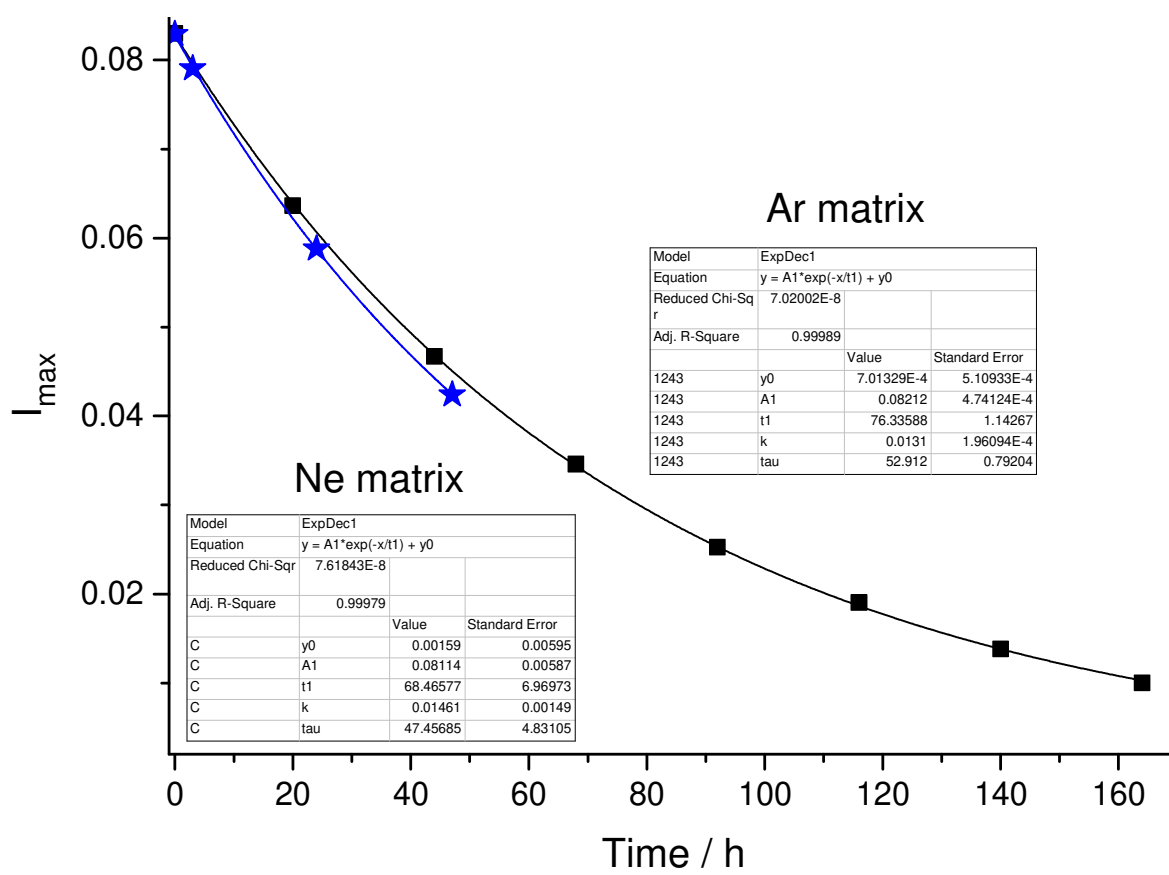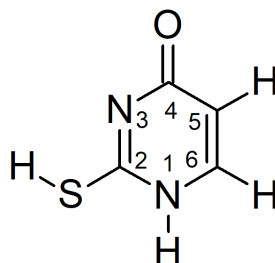
Ar matrix

Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	7.02002E-8		
Adj. R-Square	0.99989		
		Value	Standard Error
1243	y0	7.01329E-4	5.10933E-4
1243	A1	0.08212	4.74124E-4
1243	t1	76.33588	1.14267
1243	k	0.0131	1.96094E-4
1243	tau	52.912	0.79204

Ne matrix

Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	7.61843E-8		
Adj. R-Square	0.99979		
		Value	Standard Error
C	y0	0.00159	0.00595
C	A1	0.08114	0.00587
C	t1	68.46577	6.96973
C	k	0.01461	0.00149
C	tau	47.45685	4.83105

Figure S2. Progress of the spontaneous thiol $\rightarrow$ thione hydrogen-atom tunneling observed for 2-thiouracil monomers isolated in Ar and Ne matrices kept at 3.5 K and in the dark. The progress of the conversion was measured as an intensity decrease of the bands due to form **III** observed at 1243 cm^{-1} (Ar matrix) and 1646 cm^{-1} (Ne matrix).

Table S1.

The spectral positions ($\tilde{\nu}$) and relative intensities (I) of the detected IR absorption bands attributed to the oxo-thiol form **III** of 2-thiouracil. The bands are assigned to the normal modes that are theoretically predicted at the DFT(B3LYP)/6-311++G(2d,p) level for form **III**.

Ar matrix		Calculated at DFT(B3LYP)/6-311++G(2d,p) level			
$\tilde{\nu}$ cm^{-1}	I rel.	$\tilde{\nu}$ [a] cm^{-1}	A^{th} km·mol^{-1}	Symmetry	Approximate description[b]
3467	125	3484	83	A'	νN1H
2616, 2614	22	2586	11	A'	νS-H
1707sh, 1701	252	1703	455	A'	νC=O, βring
1643	71	1645	141	A'	βC6H, βN1H, βC5H, νC5=C6
1562, 1557	303	1562	456	A'	βN1H, νC2=N3
1478, 1476, 1471	122	1464	165	A'	βN1H, νC2-N1, νN1-C6
1259, 1252, 1244	175	1237	242	A'	βN1H, βC6H, νC4-N3, νC4-C5
1028	7	1053	4	A'	βN1H, βC5H, βC=S
988	30	988	37	A'	βC=S, βring
899	29	886	26	A'	βC=S, ring breath
846	4	842	6	A'	βC=S, βring
827	30	824	49	A"	γC5H, γC6H, ring torsion
694	8	686	8	A'	βring, νC-S
508	30	468	39	A"	γN1H, γC6H

The most intense components of the split bands are underlined.

[a] Theoretically predicted wavenumbers were scaled by 0.98 for wavenumbers lower than 2000 cm^{-1}, or by 0.95 for wavenumbers higher than 2000 cm^{-1}.

[b] Abbreviations: ν stretching; β bending in-plane; γ bending out-of-plane.
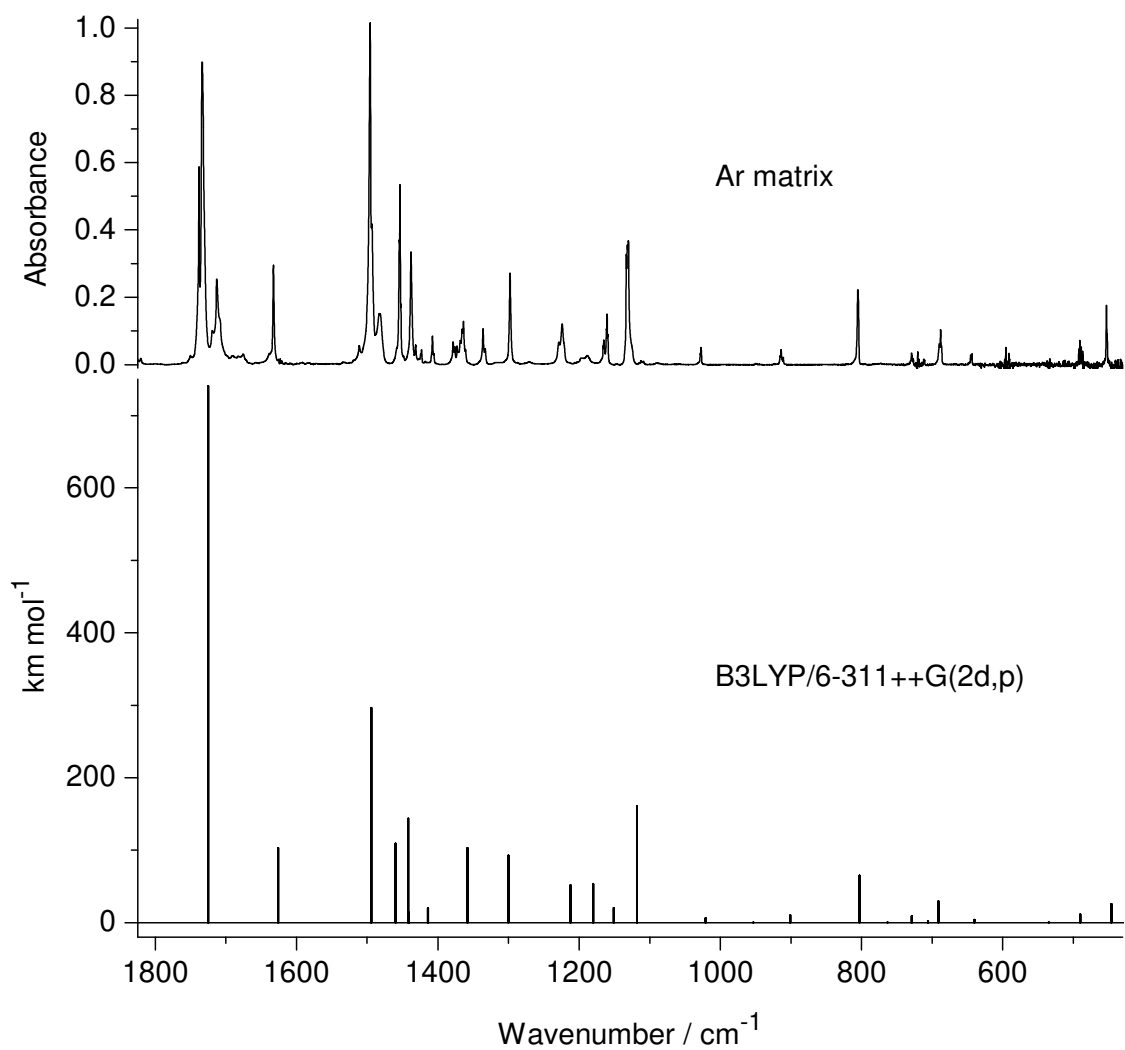
Figure S3. Infrared spectrum of 1-methyl-2-thiouracil monomers isolated in an Ar matrix compared with the theoretical spectrum calculated at the B3LYP/6-311++G(2d,p) level for the most stable oxo-thione tautomer **V**.
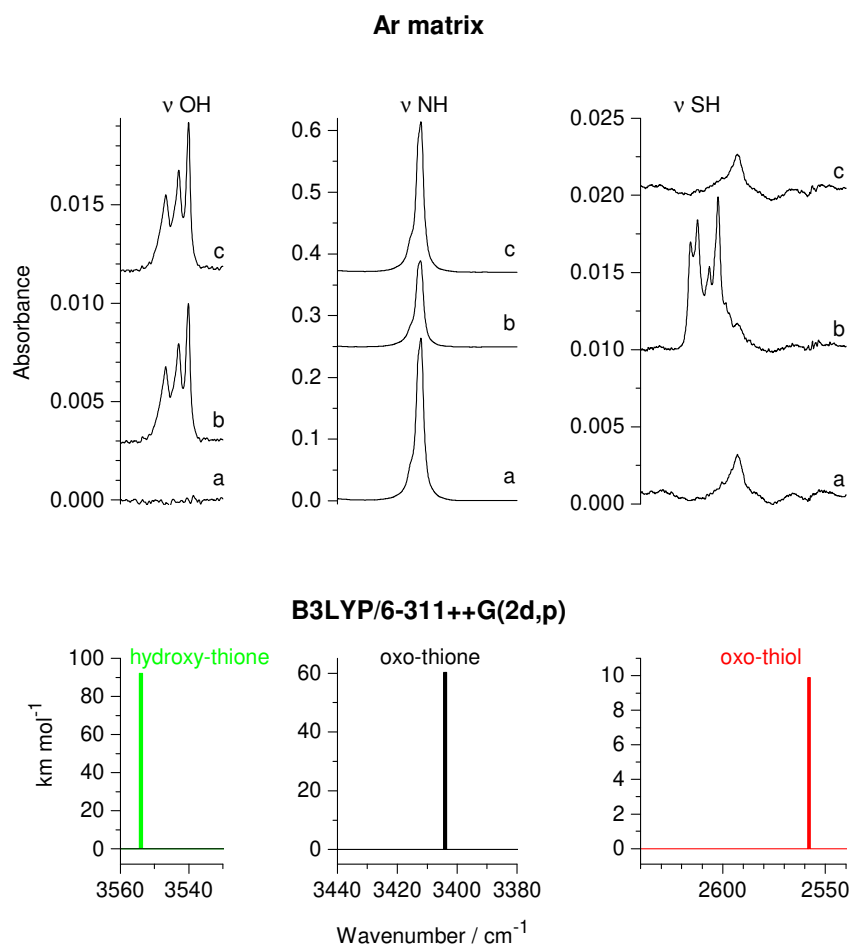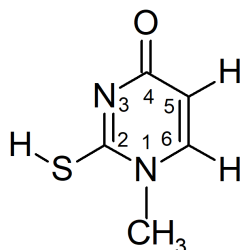
Ar matrix

B3LYP/6-311++G(2d,p)

Figure S4. High-frequency fragment of the infrared spectra of 1-methyl-2-thiouracil monomers isolated in a low-temperature Ar matrix: (a) after deposition of the matrix; (b) after 5 hours of exposure to UV(λ=305 nm) light; (c) after subsequent 16 hours when the matrix was kept at 3.5 K and in the dark; compared with the theoretical spectra simulated at the B3LYP/6-311++G(2d,p) level for: (black) the oxo-thione form **V;** (red) the oxo-thiol form **VI;** (green) the hydroxy-thiol form **VII** of the compound.

Table S2.

The spectral positions ($\tilde{\nu}$) and relative intensities (*I*) of the detected IR absorption bands attributed to the oxo-thiol form **VI** of 1-methyl-2-thiouracil. The bands are assigned to the normal modes that are theoretically predicted at the DFT(B3LYP)/6-311++G(2d,p) level for form **VI**.

Ar matrix		Calculated at DFT(B3LYP)/6-311++G(2d,p) level			
$\tilde{\nu}$ cm^{-1}	I rel.	$\tilde{\nu}$ [a] cm^{-1}	A^{th} km·mol^{-1}	Symmetry	Approximate description[b]
2961	10	2946	7	A″	νCH$_3$
2938		2890	23	A′	νCH$_3$sym
2614, 2603	20	2558	10	A′	νS-H
1690	350	1696	548	A′	νC=O, βC5H, βring
1641	150	1642	223	A′	βC6H, βC5H, νring
1510, 1506	240	1510	315	A′	βCH$_3$, βC5H, βC6H, νring
1478	80	1485	69	A′	βCH$_3$
1423	110	1413	101	A′	βC5H, βC6H, νring
1364	75	1353	154	A′	βC5H, βC6H, βCH$_3$, νring
1260	20	1243	46	A′	νC-CH$_3$, νring, βC6H
1196	20	1189	37	A′	βC5H, νC-CH$_3$, βring
1157	20	1143	45	A′	βCH$_3$, βC6H, νring
1112	70	1098	85	A′	νC-S, βS-H, βC5H, νring
927	15	927	40	A′	βS-H
825	35	823	50	A″	γC5H, γC6H, γring
697	4	690	5	A′	βring, νC-S

The most intense components of the split bands are underlined.

[a] Theoretically predicted wavenumbers were scaled by 0.98 for wavenumbers lower than 2000 cm^{-1}, or by 0.95 for wavenumbers higher than 2000 cm^{-1}.

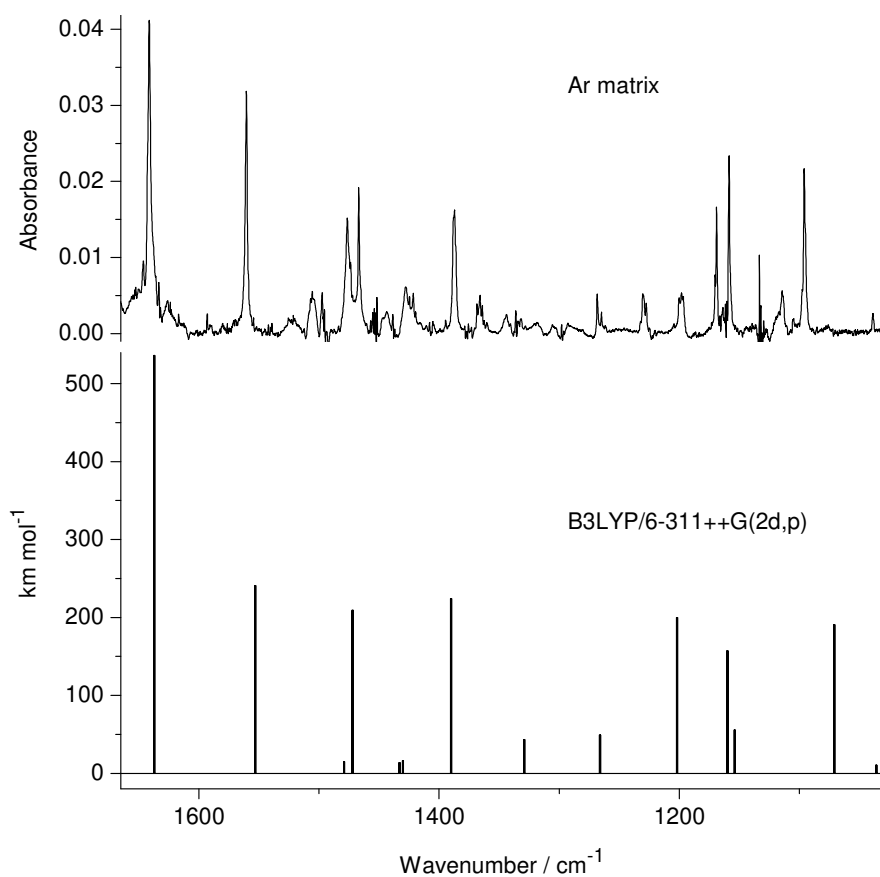[b] Abbreviations: ν stretching; β bending in-plane; γ bending out-of-plane.

Figure S5. Extracted experimental spectrum of hydroxy-thione form of 1-methyl-2-thiouracil isolated in a low-temperature Ar matrix. The low-intensity bands belonging to this spectrum appeared upon UV(λ=305 nm) irradiation of matrix-isolated 1-methyl-2-thiouracil; these bands did not decrease during the period when the matrix was kept at 3.5 K and in the dark. The theoretical spectrum simulated at the B3LYP/6-311++G(2d,p) level for the hydroxy-thione form **VII** matches well the experimental spectrum.
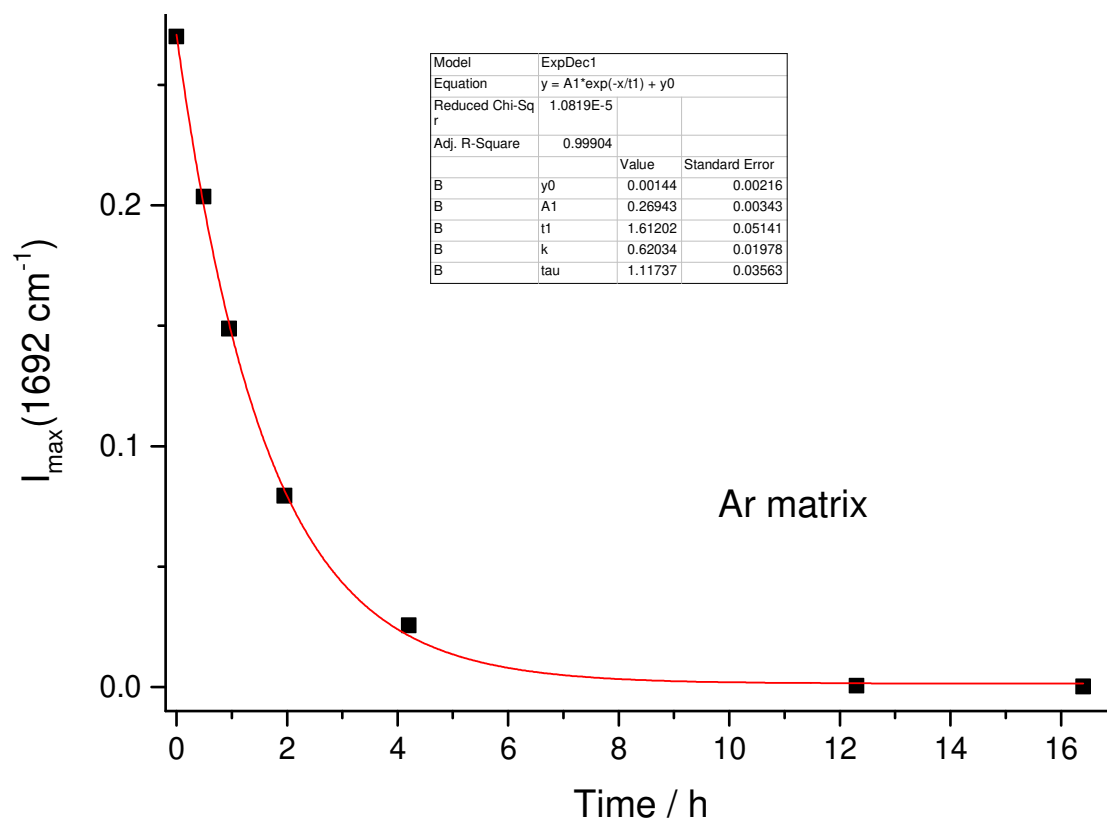
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	1.0819E-5		
Adj. R-Square	0.99904		
		Value	Standard Error
B	y0	0.00144	0.00216
B	A1	0.26943	0.00343
B	t1	1.61202	0.05141
B	k	0.62034	0.01978
B	tau	1.11737	0.03563

Ar matrix

Figure S6. Progress of the spontaneous thiol $\rightarrow$ thione hydrogen-atom tunneling observed for 1-methyl-2-thiouracil monomers isolated in an Ar matrix kept at 3.5 K and in the dark. The progress of the conversion was measured as an intensity decrease of the band due to form **VI** observed at 1692 cm^{-1}.
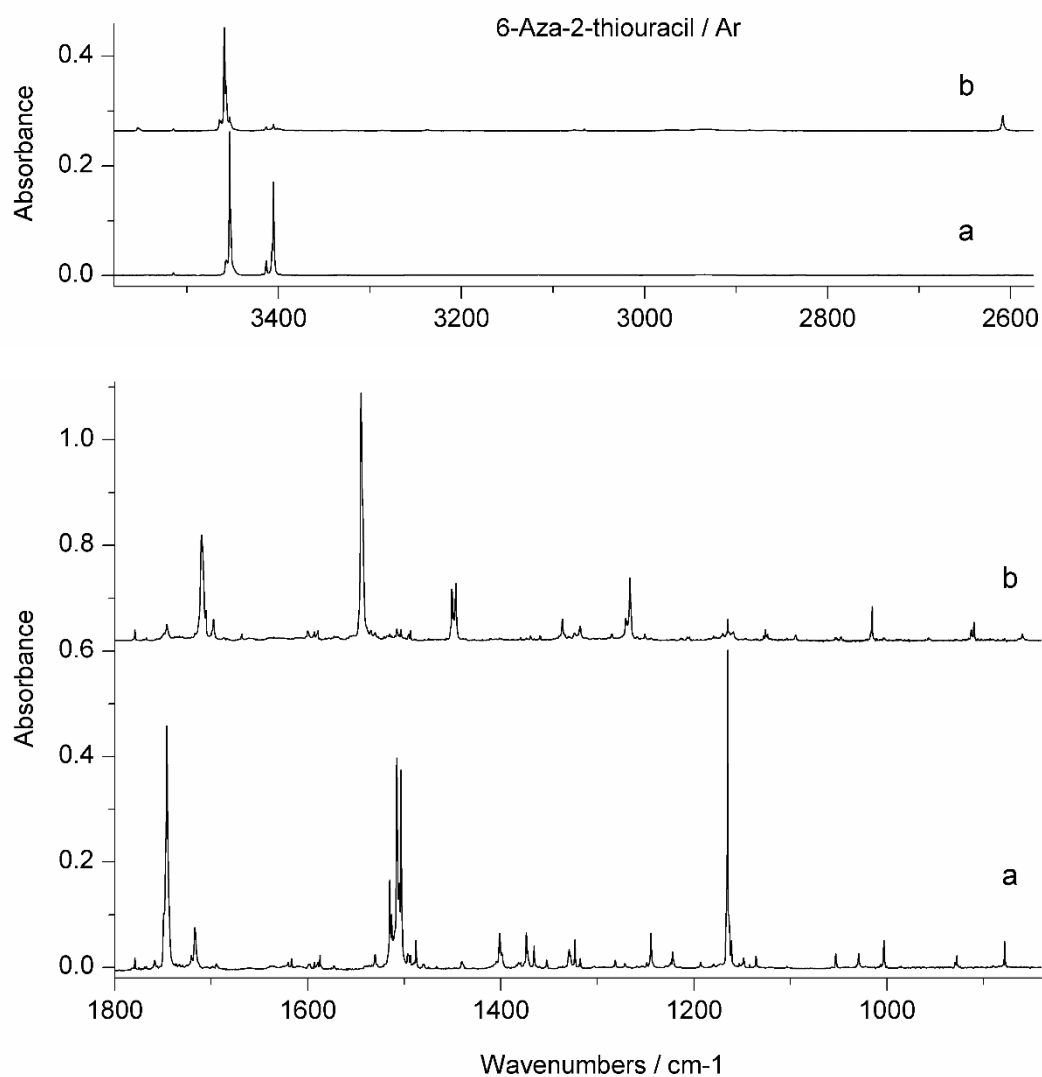
Figure S7. The effect of UV (λ=305 nm) irradiation of the Ar matrix dopped with momeric molecules of 6-aza-2-thiouracil: (a) the IR spectrum recorded after matrix formation; (b) the spectrum recorded after subsequent UV irradiation of the matrix for 6 h.
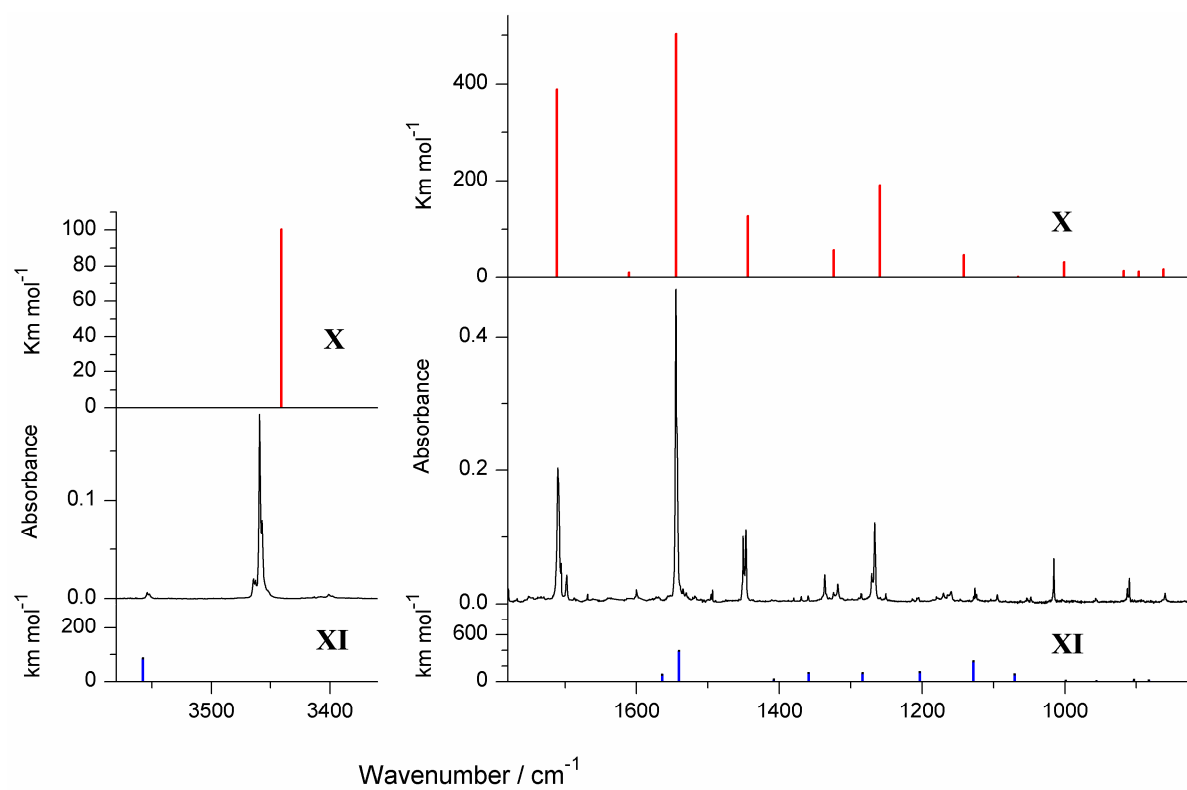
Figure S8. The spectrum of photoproducts generated upon 6h of UV(λ=305 nm) irradiation of the 6-aza-2-thiouracil monomers isolated in an Ar matrix compared with the theoretical spectra calculated for the oxo-thiol form **X** (red sticks) and for the hydroxy-thiol form **XI** (blue sticks).

Table S3.

The spectral positions ($\tilde{\nu}$) and relative intensities (I) of the detected IR absorption bands attributed to the oxo-thiol form **X** of 6-aza2-thiouracil. The bands are assigned to the normal modes that are theoretically predicted at the DFT(B3LYP)/6-311++G(2d,p) level for form **X**.
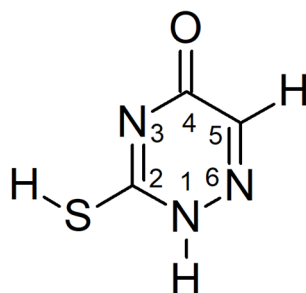
Ar matrix		Calculated at DFT(B3LYP)/6-311++G(2d,p) level			
$\tilde{\nu}$ cm^{-1}	I rel.	$\tilde{\nu}$ [a] cm^{-1}	A^{th} km·mol^{-1}	Symmetry	Approximate description[b]
3463, 3459, 3457	200	3441	101	A′	νN1H
2609	30	2555	12	A′	νS-H
1710, 1698	390	1712	389	A′	νC=O, βring, βC5H
1545	610	1545	503	A′	βN1H, νC2C3
1451, 1447	170	1444	127	A′	βN1H, βring
1336, 1318	90	1324	58	A′	βC5H, βN1H
1270, 1266	145	1259	192	A′	βC5H, βN1H, νring
1015	35	1001	33	A′	βring
913, 910	30	918	15	A″	γC5H
860	15	862	18	A′	βSH, νring
685	10	680	9	A′	βring
567	15	563	11	A′	βring
538	100	520	79	A″	γN1H

The most intense components of the split bands are underlined.

[a] Theoretically predicted wavenumbers were scaled by 0.98 for wavenumbers lower than 2000 cm^{-1}, or by 0.95 for wavenumbers higher than 2000 cm^{-1}.

[b] Abbreviations: ν stretching; β bending in-plane; γ bending out-of-plane.