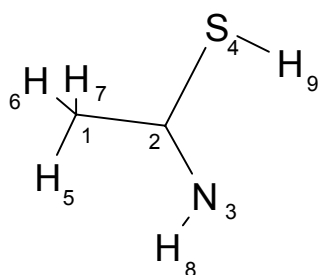
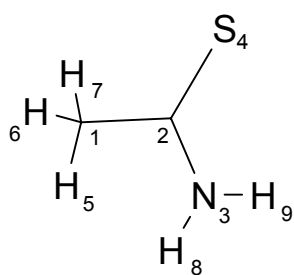


Electronic Supplementary Information:



Scheme S1. Atom numbering for thione and thiol tautomers of thioacetamide

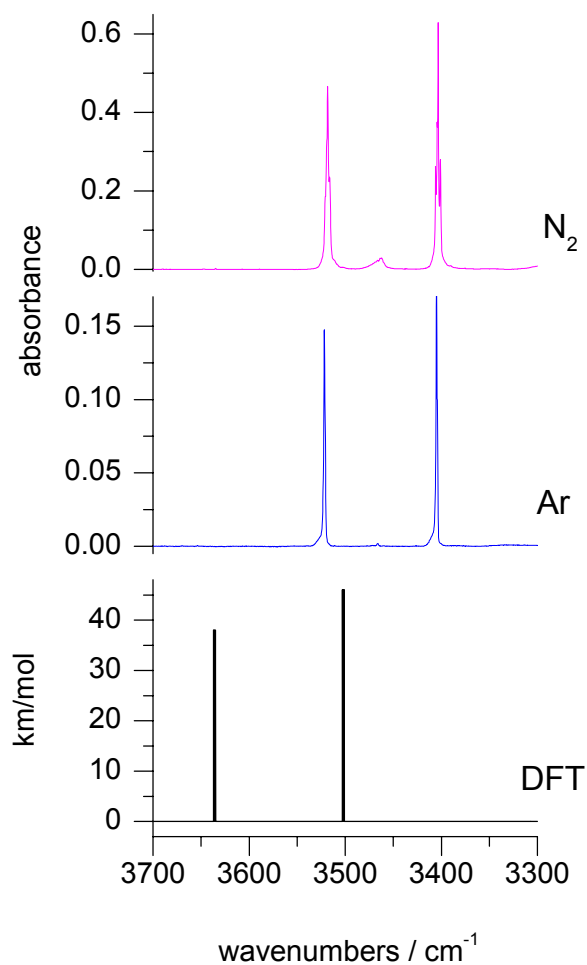


Figure S1

High frequency region of the infrared spectra of thioacetamide isolated in Ar and N_2 matrices compared with the spectrum calculated theoretically for the thione-amino tautomer **I**. Baseline of the experimental spectra was corrected; theoretical spectra were calculated at the DFT(B3LYP)/6-31++G(d,p) level, and theoretical frequencies scaled by 0.98.

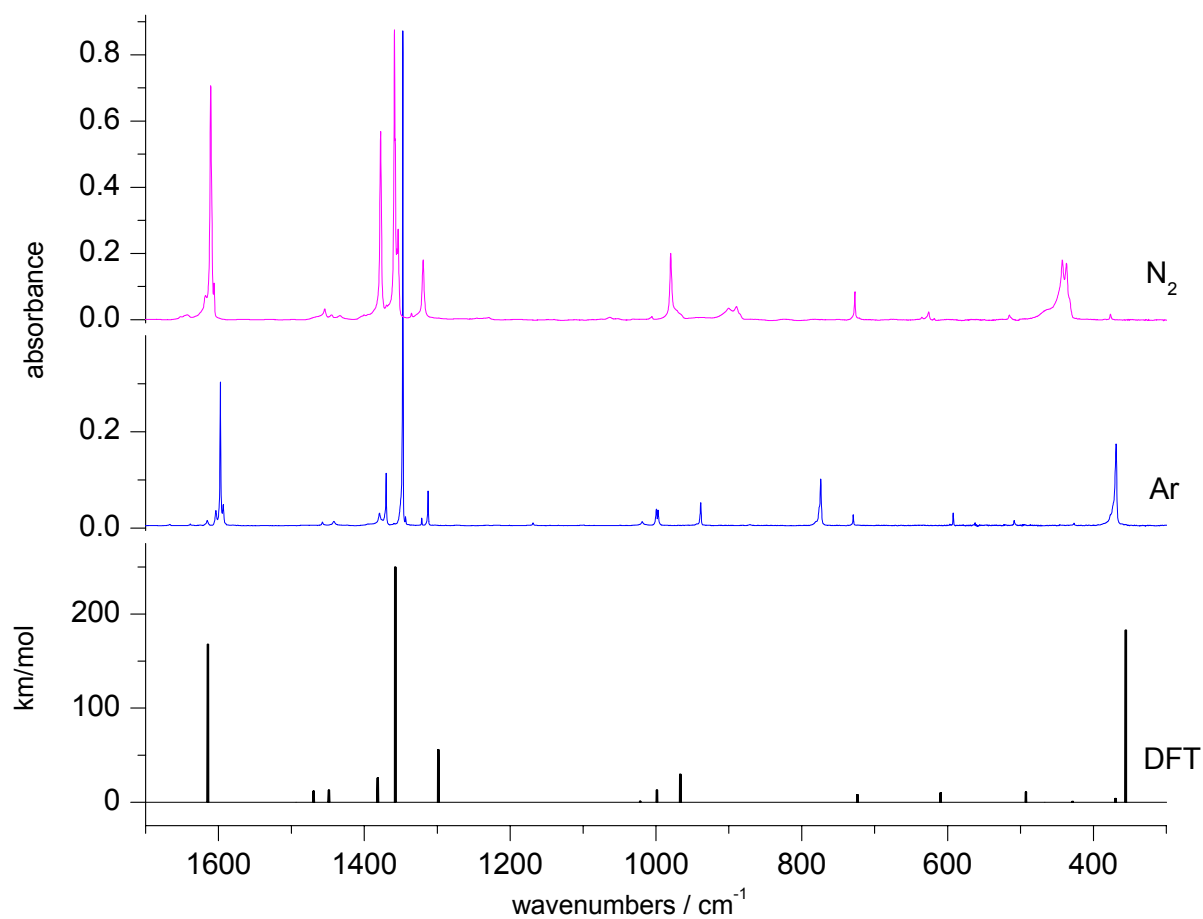


Figure S2.

The infrared spectra of thioacetamide isolated in Ar and N_2 matrices compared with the spectrum calculated theoretically for the thione-amino tautomer **I**. Baseline of the experimental spectra was corrected; theoretical spectra were calculated at the DFT(B3LYP)/6-31++G(d,p) level, and theoretical frequencies scaled by 0.98.

Table S1.

Internal coordinates used in the normal mode analysis for the thione tautomer of thioacetamide.

Atom numbering as in Scheme S1.

$S_1=(2^{-1/2})(r_{3,9} + r_{3,8})$	$\nu_s\text{NH}_2$
$S_2=(2^{-1/2})(r_{3,9} - r_{3,8})$	$\nu_a\text{NH}_2$
$S_3=r_{3,2}$	$\nu\text{ CN}$
$S_4=r_{2,4}$	$\nu\text{ C=S}$
$S_5=r_{2,1}$	$\nu\text{ CC}$
$S_6=(3^{-1/2})(r_{1,7} + r_{1,6} + r_{1,5})$	$\nu\text{ Me1}$
$S_7=(6^{-1/2})(2r_{1,5} - r_{1,7} - r_{1,6})$	$\nu\text{ Me2}$
$S_8=(2^{-1/2})(r_{1,7} - r_{1,6})$	$\nu\text{ Me3}$
$S_9=(6^{-1/2})(2\beta_{8,9,3} - \beta_{8,2,3} - \beta_{9,2,3})$	NH_2scis
$S_{10}=(2^{-1/2})(\beta_{8,2,3} - \beta_{9,2,3})$	NH_2rock
$S_{11}=(6^{-1/2})(2\beta_{3,1,2} - \beta_{3,4,2} - \beta_{1,4,2})$	$\beta\text{ CCN}$
$S_{12}=(2^{-1/2})(\beta_{3,4,2} - \beta_{1,4,2})$	$\beta\text{ C=S}$
$S_{13}=(12^{-1/2})(\beta_{7,5,1} + \beta_{7,6,1} + \beta_{5,6,1} - \beta_{7,2,1} - \beta_{5,2,1} - \beta_{6,2,1})$	$\beta\text{ Me1}$
$S_{14}=(6^{-1/2})(2\beta_{7,6,1} - \beta_{7,5,1} - \beta_{6,5,1})$	$\beta\text{ Me2}$
$S_{15}=(2^{-1/2})(\beta_{7,5,1} - \beta_{6,5,1})$	$\beta\text{ Me3}$
$S_{16}=(6^{-1/2})(2\beta_{5,2,1} - \beta_{7,2,1} - \beta_{6,2,1})$	$\beta\text{ Me4}$
$S_{17}=(2^{-1/2})(\beta_{7,2,1} - \beta_{6,2,1})$	$\beta\text{ Me5}$
$S_{18}=(12^{-1/2})(\tau_{5,1,2,4} + \tau_{5,1,2,3} + \tau_{6,1,2,4} + \tau_{6,1,2,3} + \tau_{7,1,2,4} + \tau_{7,1,2,3})$	$\tau\text{ Me}$
$S_{19}=1/2(\tau_{8,3,2,4} + \tau_{8,3,2,1} + \tau_{9,3,2,4} + \tau_{9,3,2,1})$	$\tau\text{ NH}_2$
$S_{20}=\gamma_{2,8,3,9}$	NH_2inv
$S_{21}=\gamma_{4,3,2,1}$	$\gamma\text{ C=S}$

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

Table S2.

Internal coordinates used in the normal mode analysis for the thiol tautomer of thioacetamide.

Atom numbering as in Scheme S1.

$S_1=r_{3,8}$	ν NH
$S_2=r_{4,9}$	ν SH
$S_3=r_{2,3}$	ν C=N
$S_4=r_{4,2}$	ν CS
$S_5=r_{2,1}$	ν CC
$S_6=(3^{-1/2})(r_{1,7} + r_{1,6} + r_{1,5})$	ν Me1
$S_7=(6^{-1/2})(2r_{1,5} - r_{1,7} - r_{1,6})$	ν Me2
$S_8=(2^{-1/2})(r_{1,7} - r_{1,6})$	ν Me3
$S_9=\beta_{7,2,3}$	β NH
$S_{10}=(6^{-1/2})(2\beta_{3,1,2} - \beta_{4,3,2} - \beta_{1,4,2})$	β CCN
$S_{11}=\beta_{9,2,4}$	β SH
$S_{12}=(2^{-1/2})(\beta_{4,1,2} - \beta_{4,3,2})$	β CS
$S_{13}=(12^{-1/2})(\beta_{7,5,1} + \beta_{7,6,1} + \beta_{5,6,1} - \beta_{7,2,1} - \beta_{5,2,1} - \beta_{6,2,1})$	β Me1
$S_{14}=(6^{-1/2})(2\beta_{7,6,1} - \beta_{7,5,1} - \beta_{6,5,1})$	β Me2
$S_{15}=(2^{-1/2})(\beta_{7,5,1} - \beta_{6,5,1})$	β Me3
$S_{16}=(6^{-1/2})(2\beta_{5,2,1} - \beta_{7,2,1} - \beta_{6,2,1})$	β Me4
$S_{17}=(2^{-1/2})(\beta_{7,2,1} - \beta_{6,2,1})$	β Me5
$S_{18}=(12^{-1/2})(\tau_{7,1,2,4} + \tau_{7,1,2,3} + \tau_{5,1,2,4} + \tau_{5,1,2,3} + \tau_{6,1,2,4} + \tau_{6,1,2,3})$	τ Me
$S_{19}=(2^{-1/2})(\tau_{8,3,2,4} + \tau_{8,3,2,1})$	τ NH
$S_{20}=(2^{-1/2})(\tau_{9,4,2,1} + \tau_{9,4,2,3})$	τ SH
$S_{21}=\gamma_{4,1,2,3}$	γ CS

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

Table S3. Experimental wavenumbers ($\tilde{\nu}$ / cm^{-1}) and relative integral intensities (I) of the absorption bands in the spectrum of matrix isolated thioacetamide, compared with wavenumbers ($\tilde{\nu}$ / cm^{-1}), absolute intensities (A^{th} / $\text{km}\cdot\text{mol}^{-1}$) and potential energy distribution (PED / %) theoretically calculated for the thione form **I**.

experimental				calculated		
Ar matrix		N ₂ matrix		DFT(B3LYP)/6-31++G(d,p)		
$\tilde{\nu}$ ^a	I	$\tilde{\nu}$ ^a	I	$\tilde{\nu}$ ^b	A^{th}	PED
3521	67	<u>3521</u> <u>3518</u> 3510	100	3636	38	$\nu_{\text{a}}\text{NH}_2(100)$
3466	1	3463	16			
3405	71	3406 sh <u>3404</u>	101	3502	46	$\nu_{\text{s}}\text{NH}_2(100)$
3404	sh	3401 sh				
3288	4	3288				
3176	2	3201	5			
2964	5	2966	4	3041	16	ν Me3(99)
2925	6	2926	8	2979	23	ν Me1(91)
1624						
1615						
1608						
1603		1617				
<u>1597</u>	158	<u>1610</u>	143	1614	168	$\text{NH}_2\text{scis}(90)$
<u>1593</u>		<u>1605</u>				
1457	3	1453	4	1469	12	β Me3(80)
1441	7	1443	5	1448	13	β Me2(83) β Me4(10)
		1432	6			
1378						
<u>1369</u>	68	1377	111	1381	26	β Me1(87)
<u>1347</u>	262	<u>1358</u>	179	1357	250	ν CN(54)
1343		1353 sh				
1321						
<u>1312</u>	24	1319	4	1298	56	$\text{NH}_2\text{rock}(40)$, ν CC(22), ν C=S(12)
1168	2					
1018	10	1005	1	1021	1	β Me5(42), β Me4(36), γ C=S(10)
<u>999</u>	29	979	51	998	13	β Me4(39), β Me5(30), $\text{NH}_2\text{rock}(13)$, ν CN(12)
997						
938	20	899	33	966	30	$\text{NH}_2\text{rock}(37)$, ν CC(33), ν C=S(21)
		887				
774	66					overtone of NH_2inv
729	7	727	10	723	8	ν C=S(49), ν CC(34), ν CN(10)
		637				
592	6	<u>625</u> 618	6	609	10	τ $\text{NH}_2(82)$
508	4	515	2	492	11	γ C=S(81)
426	2			428	1	β CNN(66), β C=S(19)
376	sh	376	2	369	4	β C=S(72), β CCN(17)
368	157	442	139	355	183	$\text{NH}_2\text{inv}(90)$, τ $\text{NH}_2(10)$
		437				
				64	1	τ Me(99)

^a Wavenumbers of the strongest bands are underlined.

^b Theoretical frequencies have been scaled by 0.98. PED's lower than 10% are not included.

sh - shoulder

Table S4

Normal mode frequencies ($\tilde{\nu}$), potential energy distribution (PED) and absolute intensities (A^{th}) of the theoretically predicted (DFT(B3LYP)/6-31++G(d,p)) IR bands for the form **II** of the thiol tautomer of thioacetamide.

mode No.	$\tilde{\nu}^{\text{a}}$ cm ⁻¹	A^{th} km·mol ⁻¹	PED ^b %	approximate assignment
Q1	3388	1	ν NH(100)	NH str
Q2	3071	14	ν Me2(100)	Me str
Q3	3053	5	ν Me3(100)	Me str
Q4	2985	7	ν Me1(100)	Me str
Q5	2641	1	ν SH(100)	SH str
Q6	1656	158	ν C=N(87)	C=N str
Q7	1457	23	β Me2(90)	Me bend
Q8	1449	13	β Me3(95)	Me bend
Q9	1383	18	β Me1(95)	Me umbr
Q10	1270	61	β NH(65), β CCN(11)	NH bend
Q11	1047	55	β Me4(55), β NH(26)	Me rock
Q12	1042	5	β Me5(73), τ NH(11), γ CS(85)	Me rock
Q13	981	55	β SH(34), ν CC(30), β Me4(11), ν C=N(10)	CC str, SH bend
Q14	838	14	β SH(59), ν CC(29), β Me4(10)	SH bend
Q15	806	62	τ NH(90)	NH tors
Q16	626	52	ν CS(60), β CCN(17), ν CC(14)	CS str
Q17	488	1	γ CS(89), β Me5(10)	CS wagg
Q18	441	8	β CCN(51), ν CS(27), β CS(18)	CCN bend, CS str
Q19	332	25	τ SH(96)	SH tors
Q20	321	4	β CS(75), β CCN(16)	CS bend
Q21	106	1	τ Me(98)	Me twist

^a Frequencies have been scaled by 0.98.

^b Internal coordinates used in PED analysis are defined in Table S2. PED's lower than 10% not included.

Abbreviations: str - stretching; bend - bending; umbr - umbrella; rock - rocking; tors - torsion; wagg - wagging; twist - twisting.

Table S5

Normal mode frequencies ($\tilde{\nu}$), potential energy distribution (PED) and absolute intensities (A^{th}) of the theoretically predicted (DFT(B3LYP)/6-31++G(d,p)) IR bands for the form **III** of the thiol tautomer of thioacetamide.

mode No.	$\tilde{\nu}^{\text{a}}$ cm ⁻¹	A^{th} km·mol ⁻¹	PED ^b %	approximate assignment
Q1	3402	1	v NH(100)	NH str
Q2	3066	17	v Me2(100)	Me str
Q3	3051	6	v Me3(100)	Me str
Q4	2982	8	v Me1(100)	Me str
Q5	2639	8	v SH(100)	SH str
Q6	1659	179	v C=N(88)	C=N str
Q7	1458	17	β Me2(90)	Me bend
Q8	1450	13	β Me3(93)	Me bend
Q9	1380	14	β Me1(96)	Me umbr
Q10	1270	53	β NH(63), β CCN(11)	NH bend
Q11	1041	70	β Me4(52), β NH(28)	Me rock
Q12	1040	4	β Me5(73), τ NH(12)	Me rock
Q13	997	51	β SH(51), v CC(17), β Me4(13)	CC str, SH bend
Q14	885	14	β SH(44), v CC(39), β Me4(10)	SH bend
Q15	811	67	τ NH(89)	NH tors
Q16	628	51	v CS(56), β CCN(18), v CC(18)	CS str
Q17	495	1	γ CS(87), β Me5(10)	CS wagg
Q18	427	3	β CCN(55), v CS(30), β CS(11)	CCN bend, CS str
Q19	337	1	β CS(82), β CCN(11)	CS bend
Q20	212	7	τ SH(87)	SH tors
Q21	150	1	τ Me(92)	Me twist

^a Frequencies have been scaled by 0.98.

^b Internal coordinates used in PED analysis are defined in Table S2. PED's lower than 10% not included.

Abbreviations: str - stretching; bend - bending; umbr - umbrella; rock - rocking; tors - torsion; wagg - wagging; twist - twisting.

Table S6

Normal mode frequencies ($\tilde{\nu}$), potential energy distribution (PED) and absolute intensities (A^{th}) of the theoretically predicted (DFT(B3LYP)/6-31++G(d,p)) IR bands for the form **IV** of the thiol tautomer of thioacetamide.

mode No.	$\tilde{\nu}^{\text{a}}$ cm ⁻¹	A^{th} km·mol ⁻¹	PED ^b %	approximate assignment
Q1	3414	4	ν NH(100)	NH str
Q2	3098	4	ν Me2(97)	Me str
Q3	3050	6	ν Me3(100)	Me str
Q4	2986	7	ν Me1(96)	Me str
Q5	2636	8	ν SH(100)	SH str
Q6	1670	152	ν C=N(86)	C=N str
Q7	1455	15	β Me3(92)	Me bend
Q8	1449	13	β Me2(92)	Me bend
Q9	1382	17	β Me1(94)	Me umbr
Q10	1236	233	β NH(65)	NH bend
Q11	1057	29	β Me4(57), β NH(17)	Me rock
Q12	1051	4	β Me5(75), τ NH(10)	Me rock
Q13	983	8	ν CC(35), β SH(31), β NH(14)	CC str, SH bend
Q14	858	13	β SH(61), ν CC(29)	SH bend
Q15	831	64	τ NH(88)	NH tors
Q16	603	45	ν CS(53), β CCN(28), ν CC(10)	CS str
Q17	482	3	γ CS(89), β Me5(11)	CS wagg
Q18	436	15	β CCN(40), ν CS(37), β CS(19)	CCN bend, CS str
Q19	325	3	β CS(72), β CCN(18)	CS bend
Q20	269	12	τ SH(96)	SH tors
Q21	144	2	τ Me(96)	Me twist

^a Frequencies have been scaled by 0.98.

^b Internal coordinates used in PED analysis are defined in Table S2. PED's lower than 10% not included.

Abbreviations: str - stretching; bend - bending; umbr - umbrella; rock - rocking; tors - torsion; wagg - wagging; twist - twisting.

Table S7

Normal mode frequencies ($\tilde{\nu}$), potential energy distribution (PED) and absolute intensities (A^{th}) of the theoretically predicted (DFT(B3LYP)/6-31++G(d,p)) IR bands for the form **V** of the thiol tautomer of thioacetamide.

mode No.	$\tilde{\nu}^{\text{a}}$ cm ⁻¹	A^{th} km·mol ⁻¹	PED ^b %	approximate assignment
Q1	3402	3	ν NH(100)	NH str
Q2	3093	6	ν Me2(97)	Me str
Q3	3048	8	ν Me3(100)	Me str
Q4	2986	8	ν Me1(97)	Me str
Q5	2639	5	ν SH(100)	SH str
Q6	1669	163	ν C=N(86)	C=N str
Q7	1457	15	β Me3(93)	Me bend
Q8	1449	9	β Me2(92)	Me bend
Q9	1380	15	β Me1(94)	Me umbr
Q10	1252	222	β NH(65)	NH bend
Q11	1053	27	β Me4(56), β NH(20)	Me rock
Q12	1050	5	β Me5(75), τ NH(12)	Me rock
Q13	979	6	ν CC(34), β SH(25), β Me4(14), β NH(14)	CC str, SH bend
Q14	861	9	β SH(68), ν CC(26)	SH bend
Q15	848	57	τ NH(85)	NH tors
Q16	606	37	ν CS(53), β CCN(26), ν CC(12)	CS str
Q17	485	4	γ CS(85), β Me5(10)	CS wagg
Q18	414	16	β CCN(49), ν CS(38)	CCN bend, CS str
Q19	332	1	β CS(83), β CCN(10)	CS bend
Q20	172	14	τ Me(60),	SH tors
Q21	144	8	τ SH(58), τ Me(40)	Me twist

^a Frequencies have been scaled by 0.98.

^b Internal coordinates used in PED analysis are defined in Table S2. PED's lower than 10% not included.

Abbreviations: str - stretching; bend - bending; umbr - umbrella; rock - rocking; tors - torsion; wagg - wagging; twist - twisting.

Table S8.

Optimized geometries of thione and thiol isomers of thiourea obtained at MP2/6-31++G(d,p) level of calculation.

	Isomers				
	I	II	III	IV	V
Bond lengths (Å)					
C1 - C2	1.509	1.507	1.508	1.502	1.501
C2 - N3	1.359	1.285	1.285	1.283	1.283
C2 - S4	1.643	1.772	1.776	1.790	1.791
N3 - H9	1.009				
S4 - H9		1.333	1.332	1.333	1.332
N3 - H8	1.008	1.022	1.022	1.022	1.023
C1 - H5	1.091	1.088	1.089	1.087	1.087
C1 - H6	1.092	1.091	1.090	1.090	1.091
C1 - H7	1.085	1.091	1.090	1.090	1.090
Angles (deg)					
C1 - C2 - N3	113.4	127.1	126.8	120.0	120.1
C1 - C2 - S4	123.7	113.3	117.2	112.3	116.9
C2 - S4 - H9		94.1	96.0	96.0	96.6
C2 - N3 - H9	118.7				
C2 - N3 - H8	120.9	109.3	109.5	112.2	111.7
H8 - N3 - H9	117.9				
C2 - C1 - H6	109.8	110.4	110.7	110.5	110.8
C2 - C1 - H5	110.6	110.1	109.9	108.5	108.4
C2 - C1 - H7	110.1	110.4	110.3	110.5	110.4
Dihedral angles (deg)					
C1 - C2 - N3 - S4	178.8	180.0	177.7	180.0	177.0
H8 - N3 - C2 - H9	161.7				
C1 - C2 - S4 - H9		180.0	10.1	180.0	18.3
C1 - C2 - N3 - H8	-10.6	0.0	-0.4	180.0	-179.9
N3 - C2 - C1 - H6	73.4	120.4	124.9	120.2	124.5
N3 - C2 - C1 - H5	-46.1	0.0	4.7	120.2	4.3
N3 - C2 - C1 - H7	-167.0	-120.4	-115.4	-120.2	-115.8

Table S9.

Relative electronic (ΔE_{el}), zero-point vibrational (ΔZPE), and total [$\Delta E_{\text{tot}} = \Delta E_{\text{el}} + \Delta ZPE(\text{DFT})$] energies of thioacetamide isomers.

The energy of the thione-amino **I** form was taken as reference. The calculations were carried out with 6-31++G(d,p) basis set. All data in kJ mol^{-1} .

Isomer	II	III	IV	V
$\Delta E_{\text{el}}(\text{MP2})$	48.3	57.3	48.5	49.7
$\Delta E_{\text{el}}(\text{DFT})$	54.0	62.3	54.0	54.9
$\Delta ZPE(\text{DFT})$	-9.0	-9.0	-8.9	-9.4
$\Delta E_{\text{tot}}(\text{MP2})$	39.3	48.3	39.6	40.3
$\Delta E_{\text{tot}}(\text{DFT})$	45.0	53.3	45.1	45.5