

Appendix C

Table S1. Optimized geometries for 2-methyl-2*H*-tetrazol-5-amine.^a

Parameter	B3LYP/6-311++G(d,p)
<i>Bond lengths/ pm</i>	
N ₂ N ₃	131.7
N ₂ N ₁	134.0
N ₂ C ₆	145.1
N ₃ N ₄	131.3
N ₄ C ₅	135.7
C ₅ N ₁	133.1
C ₅ N ₁₀	137.3
C ₆ H ₇	108.8
C ₆ H _{8,9}	109.1
N ₁₀ H ₁₁	100.9
N ₁₀ H ₁₂	100.9
<i>Bond angles/ degrees</i>	
N ₃ N ₂ N ₁	113.9
N ₃ N ₂ C ₆	123.1
N ₁ N ₂ C ₆	123.0
N ₂ N ₃ N ₄	106.6
N ₃ N ₄ C ₅	105.9
N ₄ C ₅ N ₁	112.6
N ₄ C ₅ N ₁₀	123.0
N ₁ C ₅ N ₁₀	124.4
N ₂ N ₁ C ₅	101.0
N ₂ C ₆ H ₇	107.3
N ₂ C ₆ H _{8,9}	109.7
H ₇ C ₆ H _{8,9}	110.3
C ₅ N ₁₀ H ₁₁	114.4
C ₅ N ₁₀ H ₁₂	115.5
H ₁₁ N ₁₀ H ₁₂	114.4
<i>Dihedral angles/ degrees</i>	
N ₁ N ₂ N ₃ N ₄	0.0
C ₆ N ₂ N ₃ N ₄	-179.9
N ₃ N ₂ N ₁ C ₅	-0.1
C ₆ N ₂ N ₁ C ₅	179.8
N ₃ N ₂ C ₆ H ₇	-0.4
N ₃ N ₂ C ₆ H ₈	119.4
N ₃ N ₂ C ₆ H ₉	-120.2
N ₂ N ₃ N ₄ C ₅	0.1
N ₃ N ₄ C ₅ N ₁	-0.2
N ₃ N ₄ C ₅ N ₁₀	177.1
N ₄ C ₅ N ₁ N ₂	0.2
N ₁₀ C ₅ N ₁ N ₂	-177.1
N ₄ C ₅ N ₁₀ H ₁₁	22.3
N ₄ C ₅ N ₁₀ H ₁₂	158.1
N ₁ C ₅ N ₁₀ H ₁₁	-160.7
N ₁ C ₅ N ₁₀ H ₁₂	-24.8

^a See Figure 1 (Chapter 3 – Part II) for atom numbering

Table S2. Definition of internal coordinates used in the normal coordinate analysis of the 2-methyl-2*H*-tetrazol-5-amine.

	Definition ^a	Approximate description
S ₁	v(C ₅ -N ₁₀)	vC-N(H ₂)
S ₂	v(N ₂ -C ₆)	vN-C(H ₃)
S ₃	v(N ₂ -N ₃)	vN ₂ -N ₃
S ₄	v(N ₃ =N ₄)	vN=N
S ₅	v(N ₄ -C ₅)	vN-C
S ₆	v(C ₅ -N ₁)	vC=N
S ₇	v(N ₁ -N ₂)	vN ₁ -N ₂
S ₈	v(C ₆ -H ₇) + v(C ₆ -H ₈) + v(C ₆ -H ₉)	vCH ₃ s
S ₉	2v(C ₆ -H ₇) - v(C ₆ -H ₈) - v(C ₆ -H ₉)	vCH ₃ as'
S ₁₀	v(C ₆ -H ₈) - v(C ₆ -H ₉)	vCH ₃ as''
S ₁₁	δ(H ₈ C ₆ H ₇) + δ(H ₇ C ₆ H ₉) + δ(H ₈ C ₆ H ₉) - δ(H ₈ C ₆ N ₂) - δ(H ₇ C ₆ N ₂) - δ(H ₉ C ₆ N ₂)	δCH ₃ s
S ₁₂	2δ(H ₈ C ₆ H ₉) - δ(H ₇ C ₆ H ₉) - δ(H ₈ C ₆ H ₇)	δCH ₃ as'
S ₁₃	δ(H ₇ C ₆ H ₉) - δ(H ₈ C ₆ H ₇)	δCH ₃ as''
S ₁₄	2δ(H ₇ C ₆ N ₂) - δ(H ₉ C ₆ N ₂) - δ(H ₈ C ₆ N ₂)	γCH ₃ '
S ₁₅	δ(H ₉ C ₆ N ₁) - δ(H ₈ C ₆ N ₁)	γCH ₃ ''
S ₁₆	δ(H ₁₁ -N ₁₀ -C ₅) + δ(H ₁₂ -N ₁₀ -C ₅)	δNH ₂
S ₁₇	δ(H ₁₁ -N ₁₀ -C ₅) - δ(H ₁₂ -N ₁₀ -C ₅)	ωNH ₂
S ₁₈	δ(N ₁₀ C ₅ N ₄) - δ(N ₁₀ C ₅ N ₁)	ωC-(NH ₂)
S ₁₉	δ(N ₄ C ₅ N ₁) - 0.809δ(N ₃ N ₄ C ₅) - 0.809δ(C ₅ N ₁ N ₂) + 0.309δ(N ₂ N ₃ N ₄) + 0.309δ(N ₁ N ₂ N ₃)	δring 1
S ₂₀	-1.118δ(N ₃ N ₄ C ₅) + 1.118δ(C ₅ N ₁ N ₂) + 1.809δ(N ₂ N ₃ N ₄) - 1.809δ(N ₁ N ₂ N ₃)	δring 2
S ₂₁	τ(H ₇ C ₆ N ₂ N ₃) + τ(H ₈ C ₆ N ₂ N ₃) + τ(H ₉ C ₆ N ₂ N ₃)	τCH ₃
S ₂₂	C ₅ out of plane N ₁₀ N ₄ (C ₅)N ₁	γring 1
S ₂₃	τ(N ₄ N ₃ N ₂ N ₁) - 0.809τ(C ₅ N ₄ N ₃ N ₂) - 0.809τ(N ₃ N ₂ N ₁ C ₅) + 0.309τ(N ₁ C ₅ N ₄ N ₃) + 0.309τ(N ₂ N ₁ C ₅ N ₄)	τring 1
S ₂₄	1.118τ(C ₅ N ₄ N ₃ N ₂) - 1.118τ(N ₃ N ₂ N ₁ C ₅) - 1.809τ(N ₁ C ₅ N ₄ N ₃) + 1.809τ(N ₂ N ₁ C ₅ N ₄)	τring 2
S ₂₅	N ₂ out of plane C ₆ N ₃ (N ₂)N ₁	γring 2
S ₂₆	δ(C ₆ N ₂ N ₃) - δ(C ₆ N ₂ N ₁)	ωN-(CH ₃)
S ₂₇	v(N ₁₀ -H ₁₁) + v(N ₁₀ -H ₁₂)	vNH ₂ s
S ₂₈	v(N ₁₀ -H ₁₁) - v(N ₁₀ -H ₁₂)	vNH ₂ as
S ₂₉	τ(H ₁₁ N ₁₀ C ₅ N ₁) + τ(H ₁₂ N ₁₀ C ₅ N ₁)	τNH ₂
S ₃₀	τ(H ₁₁ N ₁₀ C ₅ N ₁) - τ(H ₁₂ N ₁₀ C ₅ N ₁)	γNH ₂

^a See Figure 1 (Chapter 3 – Part II) for atom numbering. v, bond stretching, δ, bending, γ rocking, τ torsion, s, symmetric, as, antisymmetric. Normalizing factors (*N*) are not provided; they can be calculated as $N_j = \sqrt{\sum_i 1/c_i^2}$, where *j* refers to the vibrational coordinate and *c_i* are the coefficients associated with each coordinate in which the vibrational coordinate expands.

Table S3. DFT(B3LYP)/6-311++G(d,p) calculated frequencies and intensities, and normal coordinate analysis for 2-methyl-2*H*-tetrazol-5-amine.^a

Approximate Description	Calculated frequency	Intensity	PED ^b
νNH_2 as	3606.2	44.4	S ₂₈ (100.0)
νNH_2 s	3503.8	40.1	S ₂₇ (99.9)
νCH_3 as'	3095.6	1.1	S ₉ (97.2)
νCH_3 as''	3056.9	8.5	S ₁₀ (100.2)
νCH_3 s	2990.4	27.4	S ₈ (97.0)
δNH_2 s	1617.7	262.0	S ₁₆ (49.3) + S ₁ (19.6) + S ₃₀ (18.0)
$\nu\text{C}=\text{N}$	1541.2	136.2	S ₆ (31.0) + S ₁₆ (26.0) + S ₁ (21.8) + S ₁₉ (9.6)
δCH_3 as'	1480.3	0.7	S ₁₂ (68.3) + S ₁₄ (15.6)
δCH_3 as''	1445.2	12.1	S ₁₃ (90.5) + S ₁₅ (9.6)
$\nu\text{N}-\text{C}$	1433.4	55.6	S ₅ (24.1) + S ₁₇ (17.2) + S ₁₂ (10.8) + S ₁₈ (9.8) + S ₄ (9.6)
δCH_3 s	1417.9	0.6	S ₁₁ (89.0)
$\nu\text{N}-\text{C}(\text{H}_3)$	1381.5	11.6	S ₂ (38.9) + S ₂₀ (17.5) + S ₇ (16.1) + S ₃ (13.1)
$\nu\text{N}-\text{N}$ as	1292.1	4.3	S ₃ (29.1) + S ₁₄ (22.8) + S ₇ (17.1) + S ₁₂ (10.2)
$\nu\text{N}=\text{N}$	1226.9	39.9	S ₄ (67.4) + S ₂₀ (19.4)
$\gamma\text{CH}_3''$	1119.9	<0.1	S ₁₅ (88.4) + S ₁₃ (9.6)
ωNH_2	1090.7	2.9	S ₁₇ (31.9) + S ₆ (35.8) + S ₁₉ (9.9)
$\delta\text{ring 2}$	1073.8	11.4	S ₂₀ (20.4) + S ₁₇ (21.5) + S ₇ (12.6) + S ₁₉ (12.6) + S ₅ (14.1)
$\gamma\text{CH}_3'$	1025.3	11.8	S ₁₄ (50.3) + S ₃ (21.1) + S ₇ (11.4)
$\nu\text{N}-\text{N}$ s	1002.7	20.4	S ₇ (23.9) + S ₅ (38.6) + S ₁₉ (10.5) + S ₃ (10.3)
$\nu\text{C}-\text{N}(\text{H}_2)$	792.6	12.2	S ₁ (22.0) + S ₁₉ (24.5) + S ₂ (19.7) + S ₂₀ (14.2)
$\tau\text{ring 2}$	751.4	16.7	S ₂₄ (53.2) + S ₂₂ (40.2)
$\tau\text{ring 1}$	653.2	5.2	S ₂₃ (98.2)
$\delta\text{ring 1}$	646.5	6.2	S ₁₉ (20.1) + S ₂ (32.7) + S ₁ (12.8) + S ₂₀ (11.8)
γNH_2	540.8	267.5	S ₃₀ (71.2) + S ₁₆ (18.4)
$\omega\text{C}-(\text{NH}_2)$	455.2	0.6	S ₁₈ (51.9) + S ₂₆ (35.9)
$\gamma\text{ring 1}$	340.5	8.4	S ₂₂ (43.6) + S ₂₄ (30.3) + S ₂₅ (19.7)
τNH_2	310.7	2.7	S ₂₉ (51.8) + S ₁₈ (10.7) + S ₂₆ (27.1)
$\omega\text{N}-(\text{CH}_3)$	279.2	28.1	S ₂₆ (24.1) + S ₂₉ (42.9) + S ₁₈ (23.6)
$\gamma\text{ring 2}$	173.7	8.6	S ₂₅ (82.3) + S ₂₂ (9.7) + S ₂₄ (9.7)
τCH_3	103.8	<0.1	S ₂₁ (100.9)

^a Frequencies in cm^{-1} , calculated intensities in km mol^{-1} . ν , bond stretching, δ , bending, γ rocking, τ torsion, s, symmetric, as, antisymmetric. See Table S2 for definition of symmetry coordinates.

^b Only PED values greater than 9.5 % are given.

Table S4. Definition of internal coordinates used in the normal coordinate analysis of the six imine (aminide) tautomers of 2-methyl-2*H*-tetrazol-5-amine.

	Definition ^a	Approximate description
S ₁	$\nu(\text{C}_5\text{-N}_{10})$	$\nu\text{C-N}(\text{H}_{(11)})$
S ₂	$\nu(\text{N-H}_{12})$	$\nu\text{N-H}_{(12)}$
S ₃	$\nu(\text{N}_2\text{-C}_6)$	$\nu\text{N-C}(\text{H}_3)$
S ₄	$\nu(\text{N}_2\text{-N}_3)$	$\nu\text{N}_{(2)}\text{-N}_{(3)}$
S ₅	$\nu(\text{N}_3\text{-N}_4)$	$\nu\text{N}_{(3)}\text{-N}_{(4)}$
S ₆	$\nu(\text{N}_4\text{-C}_5)$	$\nu\text{N}_{(4)}\text{-C}_{(5)}$
S ₇	$\nu(\text{N}_1\text{-C}_5)$	$\nu\text{N}_{(1)}\text{-C}_{(5)}$
S ₈	$\nu(\text{N}_1\text{-N}_2)$	$\nu\text{N}_{(1)}\text{-N}_{(2)}$
S ₉	$\nu(\text{C}_6\text{-H}_7) + \nu(\text{C}_6\text{-H}_8) + \nu(\text{C}_6\text{-H}_9)$	νCH_3 s
S ₁₀	$2\nu(\text{C}_6\text{-H}_7) - \nu(\text{C}_6\text{-H}_8) - \nu(\text{C}_6\text{-H}_9)$	νCH_3 as'
S ₁₁	$\nu(\text{C}_6\text{-H}_8) - \nu(\text{C}_6\text{-H}_9)$	νCH_3 as''
S ₁₂	$\delta(\text{H}_8\text{C}_6\text{H}_7) + \delta(\text{H}_7\text{C}_6\text{H}_9) + \delta(\text{H}_8\text{C}_6\text{H}_9) - \delta(\text{H}_8\text{C}_6\text{N}_2) - \delta(\text{H}_7\text{C}_6\text{N}_2) - \delta(\text{H}_9\text{C}_6\text{N}_2)$	δCH_3 s
S ₁₃	$2\delta(\text{H}_8\text{C}_6\text{H}_9) - \delta(\text{H}_7\text{C}_6\text{H}_9) - \delta(\text{H}_8\text{C}_6\text{H}_7)$	δCH_3 as'
S ₁₄	$\delta(\text{H}_7\text{C}_6\text{H}_9) - \delta(\text{H}_8\text{C}_6\text{H}_7)$	δCH_3 as''
S ₁₅	$2\delta(\text{H}_7\text{C}_6\text{N}_2) - \delta(\text{H}_9\text{C}_6\text{N}_2) - \delta(\text{H}_8\text{C}_6\text{N}_2)$	$\gamma\text{CH}_3'$
S ₁₆	$\delta(\text{H}_9\text{C}_6\text{N}_2) - \delta(\text{H}_8\text{C}_6\text{N}_2)$	$\gamma\text{CH}_3''$
S ₁₇	$\delta(\text{H}_{12}\text{-N}_{4/2/3}\text{-N}_{3/1/2}) - \delta(\text{H}_{12}\text{-N}_{4/5/3}\text{-X}_{5/1/4})$ with X= C or N	$\delta\text{NH}_{(12)}$
S ₁₈	$\delta(\text{N}_{10}\text{C}_5\text{N}_4) - \delta(\text{N}_{10}\text{C}_5\text{N}_1)$	$\omega\text{C-N}(\text{H}_{(11)})$
S ₁₉	$\delta(\text{N}_4\text{C}_5\text{N}_1) - 0.809\delta(\text{N}_3\text{N}_4\text{C}_5) - 0.809\delta(\text{C}_5\text{N}_1\text{N}_5) + 0.309\delta(\text{N}_2\text{N}_3\text{N}_4) + 0.309\delta(\text{N}_1\text{N}_2\text{N}_3)$	$\delta\text{ring 1}$
S ₂₀	$-1.118\delta(\text{N}_3\text{N}_4\text{C}_5) + 1.118\delta(\text{C}_5\text{N}_1\text{N}_2) + 1.809\delta(\text{N}_2\text{N}_3\text{N}_4) - 1.809\delta(\text{N}_1\text{N}_2\text{N}_3)$	$\delta\text{ring 2}$
S ₂₁	$\tau(\text{H}_7\text{C}_6\text{N}_2\text{N}_3) + \tau(\text{H}_8\text{C}_6\text{N}_2\text{N}_3) + \tau(\text{H}_9\text{C}_6\text{N}_2\text{N}_3)$	τCH_3
S ₂₂	H_{12} out of plane $\text{N}_{3/2/2}\text{N}_{4/1/3}(\text{H}_{12})\text{X}_{5/5/4}$ with X= C or N	$\gamma\text{N-H}_{(12)}$
S ₂₃	C_5 out of plane $\text{N}_{10}\text{N}_4(\text{C}_5)\text{N}_1$	$\gamma\text{ring 1}$
S ₂₄	$\tau(\text{N}_4\text{N}_3\text{N}_2\text{N}_1) - 0.809\tau(\text{C}_5\text{N}_4\text{N}_3\text{N}_2) - 0.809\tau(\text{N}_3\text{N}_2\text{N}_1\text{C}_5) + 0.309\tau(\text{N}_1\text{C}_5\text{N}_4\text{N}_3) + 0.309\tau(\text{N}_2\text{N}_1\text{C}_5\text{N}_4)$	$\tau\text{ring 1}$
S ₂₅	$1.118\tau(\text{C}_5\text{N}_4\text{N}_3\text{N}_2) - 1.118\tau(\text{N}_3\text{N}_2\text{N}_1\text{C}_5) - 1.809\tau(\text{N}_1\text{C}_5\text{N}_4\text{N}_3) + 1.809\tau(\text{N}_2\text{N}_1\text{C}_5\text{N}_4)$	$\tau\text{ring 2}$
S ₂₆	N_2 out of plane $\text{C}_6\text{N}_3(\text{N}_2)\text{N}_1$	$\gamma\text{ring 2}$
S ₂₇	$\delta(\text{C}_6\text{N}_2\text{N}_3) - \delta(\text{C}_6\text{N}_2\text{N}_1)$	$\omega\text{N-(CH}_3)$
S ₂₈	$\nu(\text{N}_{10}\text{-H}_{11})$	$\nu\text{N-H}_{(11)}$
S ₂₉	$\tau(\text{H}_{11}\text{N}_{10}\text{C}_4\text{N}_1)$	$\tau\text{NH}_{(11)}$
S ₃₀	$\delta(\text{H}_{11}\text{N}_{10}\text{C}_5)$	$\delta\text{N-H}_{(11)}$

^a Numbering of the atoms in the tetrazole ring follows that used for 2MTA. ν , bond stretching, δ , bending, γ rocking, τ torsion, s, symmetric, as, antisymmetric. Normalizing factors (N) are not provided; they can be calculated as $N_j = \sqrt{\sum_i \frac{1}{c_i^2}}$, where j refers to the vibrational coordinate and c_i are the coefficients associated with each coordinate in which the vibrational coordinate expands.

Table S5. DFT(B3LYP)/6-311++G(d,p) calculated frequencies and intensities, and normal coordinate analysis for 3-methyl-1*H*-tetrazol-3-ium-5-aminide (A).^a

Approximate Description	Calculated frequency	Intensity	PED ^b
$\nu\text{N-H}_{(12)}$	3588.0	118.2	S ₂ (99.6)
$\nu\text{N-H}_{(11)}$	3469.4	18.1	S ₂₈ (99.8)
νCH_3 as'	3106.2	0.8	S ₁₀ (98.7)
νCH_3 as''	3075.3	2.9	S ₁₁ (100.2)
νCH_3 s	3001.8	13.4	S ₉ (98.6)
$\nu\text{C-N}(\text{H}_{(11)})$	1680.8	720.8	S ₁ (70.4) + S ₁₉ (10.0)
$\nu\text{N}_{(2)}\text{-N}_{(3)}$	1495.6	0.4	S ₄ (27.2) + S ₁₃ (39.5) + S ₁₅ (18.5)
δCH_3 as''	1441.0	14.3	S ₁₄ (89.5) + S ₁₆ (10.6)
δCH_3 as'	1434.9	12.4	S ₁₃ (44.3) + S ₄ (26.2) + S ₁₂ (14.0)
δCH_3 s	1412.8	7.5	S ₁₂ (81.0)
$\delta\text{NH}_{(12)}$	1370.6	27.0	S ₁₇ (42.5) + S ₂₀ (24.2) + S ₃ (15.5)
$\nu\text{N}_{(1)}\text{-N}_{(2)}$	1360.4	36.7	S ₈ (34.4) + S ₅ (22.1) + S ₃ (11.6)
$\delta\text{N-H}_{(11)}$	1299.9	67.1	S ₃₀ (29.4) + S ₅ (17.0) + S ₁₈ (15.0) + S ₇ (11.6) + S ₆ (11.4)
$\nu\text{N}_{(3)}\text{-N}_{(4)}$	1154.4	74.6	S ₅ (28.2) + S ₃₀ (27.5) + S ₁₅ (23.1)
$\gamma\text{CH}_3'$	1123.8	0.0	S ₁₆ (86.2) + S ₁₄ (10.6)
$\delta\text{ring 2}$	1054.0	30.2	S ₂₀ (24.9) + S ₄ (20.2) + S ₅ (14.9) + S ₁₇ (11.5) + S ₁₅ (10.9)
$\gamma\text{CH}_3'$	1044.4	100.4	S ₁₅ (28.5) + S ₈ (33.9) + S ₃₀ (17.9)
$\nu\text{N}_{(1)}\text{-C}_{(5)}$	1014.7	3.4	S ₇ (58.3)
$\nu\text{N}_{(4)}\text{-C}_{(5)}$	940.1	52.9	S ₆ (52.6) + S ₁₉ (24.5)
$\delta\text{ring 1}$	792.7	16.9	S ₁₉ (32.1) + S ₆ (19.5) + S ₃ (18.1) + S ₂₀ (13.8)
$\tau\text{NH}_{(11)}$	703.8	28.7	S ₂₉ (45.1) + S ₂₃ (36.7) + S ₂₅ (19.3)
$\gamma\text{ring 1}$	674.1	19.5	S ₂₃ (38.1) + S ₂₉ (37.2) + S ₂₄ (22.9)
$\nu\text{N-C}(\text{H}_3)$	643.2	20.0	S ₃ (37.7) + S ₁₉ (25.0) + S ₂₀ (14.6)
$\tau\text{ring 1}$	626.6	44.8	S ₂₄ (75.9) + S ₂₉ (18.9)
$\omega\text{C-N}(\text{H}_{(11)})$	482.7	14.0	S ₁₈ (55.2) + S ₂₇ (32.0)
$\gamma\text{N-H}_{(12)}$	451.1	99.0	S ₂₂ (89.2) + S ₂₃ (11.0)
$\omega\text{N-(CH}_3)$	310.8	2.1	S ₂₇ (54.8) + S ₁₈ (25.8)
$\gamma\text{ring 2}$	270.5	3.1	S ₂₆ (60.9) + S ₂₅ (12.2) + S ₂₄ (14.9)
$\tau\text{ring 2}$	163.9	4.7	S ₂₅ (66.4) + S ₂₆ (29.7)
τCH_3	109.9	0.0	S ₂₁ (101.2)

^a Frequencies in cm^{-1} , calculated intensities in km mol^{-1} . ν , bond stretching, δ , bending, γ rocking, τ torsion, s, symmetric, as, antisymmetric. See Table S4 for definition of coordinates. Numbering of the atoms in the tetrazole ring follows that used for 2MTA

^b Only PED values greater than 9.5 % are given.

Table S6. DFT(B3LYP)/6-311++G(d,p) calculated frequencies and intensities, and normal coordinate analysis for 3-methyl-1*H*-tetrazol-3-ium-5-aminide (B).^a

Approximate Description	Calculated frequency	Intensity	PED ^b
$\nu\text{N-H}_{(12)}$	3587.3	93.3	S ₂ (99.6)
$\nu\text{N-H}_{(11)}$	3449.9	11.6	S ₂₈ (99.8)
νCH_3 as'	3108.0	0.7	S ₁₀ (98.9)
νCH_3 as''	3078.7	2.3	S ₁₁ (100.2)
νCH_3 s	3004.0	11.4	S ₉ (98.7)
$\nu\text{C-N}_{(H_{(11)})}$	1678.1	693.7	S ₁ (68.5) + S ₁₉ (9.6)
δCH_3 as'	1494.6	5.1	S ₁₃ (40.9) + S ₄ (25.8) + S ₁₅ (19.0)
δCH_3 as''	1441.1	14.1	S ₁₄ (89.3) + S ₁₆ (10.7)
$\nu\text{N}_{(2)}\text{-N}_{(3)}$	1433.8	14.8	S ₄ (25.1) + S ₁₃ (39.5) + S ₁₂ (18.9)
δCH_3 s	1412.7	21.8	S ₁₂ (75.1)
$\nu\text{N}_{(1)}\text{-N}_{(2)}$	1381.8	56.7	S ₈ (25.8) + S ₂₀ (27.7) + S ₃ (25.3) + S ₁₇ (13.7)
$\delta\text{NH}_{(12)}$	1358.2	11.8	S ₁₇ (45.8) + S ₈ (16.2) + S ₅ (15.8)
$\delta\text{N-H}_{(11)}$	1275.5	66.0	S ₃₀ (26.4) + S ₅ (18.3) + S ₇ (14.6) + S ₁₈ (13.3)
$\nu\text{N}_{(3)}\text{-N}_{(4)}$	1136.6	49.2	S ₅ (33.3) + S ₃₀ (28.8) + S ₁₅ (23.2)
$\gamma\text{CH}_3''$	1124.7	0.0	S ₁₆ (85.8) + S ₁₄ (10.7)
$\gamma\text{CH}_3'$	1062.7	38.8	S ₁₅ (27.7) + S ₈ (27.1) + S ₅ (14.4) + S ₇ (12.9)
δ ring 2	1041.8	54.8	S ₂₀ (32.0) + S ₄ (24.3) + S ₁₇ (12.5)
$\nu\text{N}_{(1)}\text{-C}_{(5)}$	1012.4	130.6	S ₇ (51.7) + S ₃₀ (31.3)
$\nu\text{N}_{(4)}\text{-C}_{(5)}$	922.4	10.3	S ₆ (54.0) + S ₁₉ (26.3)
δ ring 1	784.7	2.4	S ₁₉ (29.8) + S ₆ (23.1) + S ₃ (16.7) + S ₂₀ (14.3) + S ₁ (10.1)
γ ring 1	691.4	2.1	S ₂₃ (72.4) + S ₂₅ (21.8)
τ ring 1	654.3	63.2	S ₂₄ (53.4) + S ₂₉ (44.0)
$\nu\text{N-C}_{(H_3)}$	645.8	13.5	S ₃ (38.2) + S ₁₉ (25.5) + S ₂₀ (13.8)
$\tau\text{NH}_{(11)}$	606.6	25.5	S ₂₉ (51.0) + S ₂₄ (39.2) + S ₂₃ (9.6)
$\omega\text{C-N}_{(H_{(11)})}$	495.4	10.7	S ₁₈ (57.3) + S ₂₇ (28.8)
$\gamma\text{N-H}_{(12)}$	391.3	78.8	S ₂₂ (77.0) + S ₂₃ (14.3) + S ₂₆ (13.2)
$\omega\text{N-CH}_3$	315.2	13.3	S ₂₇ (57.8) + S ₁₈ (23.3)
γ ring 2	264.7	6.0	S ₂₆ (55.5) + S ₂₂ (19.9) + S ₂₄ (19.5)
τ ring 2	166.5	14.0	S ₂₅ (70.5) + S ₂₆ (27.0)
τCH_3	104.5	0.2	S ₂₁ (100.8)

^a Frequencies in cm^{-1} , calculated intensities in km mol^{-1} . ν , bond stretching, δ , bending, γ rocking, τ torsion, s, symmetric, as, antisymmetric. See Table S4 for definition of coordinates. Numbering of the atoms in the tetrazole ring follows that used for 2MTA

^b Only PED values greater than 9.5 % are given.

Table S7. DFT(B3LYP)/6-311++G(d,p) calculated frequencies and intensities, and normal coordinate analysis for 2-methyl-1,2-dihydro-5*H*-tetrazol-5-imine (A).^a

Approximate Description	Calculated frequency	Intensity	PED ^b
$\nu\text{N-H}_{(12)}$	3482.0	45.2	$\text{S}_2(99.8)$
$\nu\text{N-H}_{(11)}$	3428.9	13.9	$\text{S}_{28}(99.8)$
νCH_3 as'	3083.5	3.0	$\text{S}_{10}(92.6)$
νCH_3 as''	3045.9	14.2	$\text{S}_{11}(85.3) + \text{S}_9(12.2)$
νCH_3 s	2965.2	43.0	$\text{S}_9(85.5) + \text{S}_{11}(9.7)$
$\nu\text{C-N}(\text{H}_{(11)})$	1688.6	351.6	$\text{S}_1(79.8)$
$\nu\text{N}_{(3)}\text{-N}_{(4)}$	1477.9	101.6	$\text{S}_5(85.4)$
δCH_3 as'	1474.6	16.1	$\text{S}_{13}(76.7) + \text{S}_{15}(11.2)$
δCH_3 as''	1446.7	31.0	$\text{S}_{14}(87.5)$
δCH_3 s	1412.3	5.2	$\text{S}_{12}(88.1)$
$\delta\text{NH}_{(12)}$	1342.8	13.1	$\text{S}_{17}(76.6)$
$\delta\text{N-H}_{(11)}$	1263.4	16.1	$\text{S}_{30}(39.2) + \text{S}_{20}(12.0) + \text{S}_6(11.6) + \text{S}_{18}(11.0)$
$\nu\text{N}_{(1)}\text{-N}_{(2)}$	1228.6	7.13	$\text{S}_3(34.8) + \text{S}_{20}(22.7) + \text{S}_8(22.0)$
$\gamma\text{CH}_3'$	1203.4	98.4	$\text{S}_{15}(35.3) + \text{S}_4(18.5)$
$\gamma\text{CH}_3''$	1116.5	32.3	$\text{S}_{16}(84.9)$
$\delta\text{ring 2}$	1042.3	25.5	$\text{S}_{20}(15.5) + \text{S}_3(40.2) + \text{S}_7(14.0) + \text{S}_4(10.4)$
$\delta\text{ring 1}$	980.9	83.6	$\text{S}_{19}(18.5) + \text{S}_{15}(27.0) + \text{S}_8(17.5) + \text{S}_4(16.5) + \text{S}_{22}(11.3)$
$\nu\text{N}_{(1)}\text{-C}_{(5)}$	947.5	23.4	$\text{S}_7(40.0) + \text{S}_8(26.1)$
$\nu\text{N}_{(2)}\text{-N}_{(3)}$	877.9	71.0	$\text{S}_6(37.5) + \text{S}_4(25.3)$
$\nu\text{N}_{(4)}\text{-C}_{(5)}$	783.9	43.6	$\text{S}_6(25.1) + \text{S}_{29}(13.7) + \text{S}_{19}(10.6) + \text{S}_{20}(9.9)$
$\tau\text{NH}_{(11)}$	779.0	51.4	$\text{S}_{29}(83.7)$
$\gamma\text{ring 1}$	753.2	16.7	$\text{S}_{23}(52.8) + \text{S}_{25}(24.0) + \text{S}_{24}(10.7)$
$\nu\text{N-C}(\text{H}_3)$	677.9	63.6	$\text{S}_8(14.9) + \text{S}_3(24.2) + \text{S}_{22}(15.6) + \text{S}_{24}(12.4) + \text{S}_{20}(9.9)$
$\tau\text{ring 1}$	581.4	108.8	$\text{S}_{24}(28.1) + \text{S}_{19}(25.5) + \text{S}_{22}(16.9) + \text{S}_3(11.1)$
$\gamma\text{N-H}_{(12)}$	521.4	23.7	$\text{S}_{22}(20.6) + \text{S}_{24}(29.4) + \text{S}_{23}(28.4)$
$\omega\text{C-N}(\text{H}_{(11)})$	480.2	18.3	$\text{S}_{18}(61.6) + \text{S}_{27}(13.9)$
$\omega\text{N-(CH}_3)$	322.9	4.2	$\text{S}_{27}(49.5) + \text{S}_{26}(13.5) + \text{S}_{18}(10.6)$
$\tau\text{ring 2}$	257.2	24.1	$\text{S}_{25}(25.2) + \text{S}_{26}(36.2) + \text{S}_{27}(15.1) + \text{S}_{21}(10.0)$
τCH_3	192.9	2.5	$\text{S}_{21}(89.6) + \text{S}_{25}(11.4)$
$\gamma\text{ring 2}$	129.4	10.7	$\text{S}_{26}(46.5) + \text{S}_{25}(34.6) + \text{S}_{24}(12.4)$

^a Frequencies in cm^{-1} , calculated intensities in km mol^{-1} . ν , bond stretching, δ , bending, γ rocking, τ torsion, s, symmetric, as, antisymmetric. See Table S4 for definition of coordinates. Numbering of the atoms in the tetrazole ring follows that used for 2MTA

^b Only PED values greater than 9.5 % are given.

Table S8. DFT(B3LYP)/6-311++G(d,p) calculated frequencies and intensities, and normal coordinate analysis for 2-methyl-1,2-dihydro-5*H*-tetrazol-5-imine (B).^a

Approximate Description	Calculated frequency	Intensity	PED ^b
$\nu\text{N-H}_{(12)}$	3496.9	54.2	$\text{S}_2(99.7)$
$\nu\text{N-H}_{(11)}$	3447.3	25.5	$\text{S}_{28}(99.7)$
νCH_3 as'	3085.4	2.4	$\text{S}_{10}(93.4)$
νCH_3 as''	3046.2	13.0	$\text{S}_{11}(87.2) + \text{S}_9(11.1)$
νCH_3 s	2967.0	42.4	$\text{S}_9(86.2)$
$\nu\text{C-N(H}_{(11)})$	1698.0	396.3	$\text{S}_1(78.7)$
δCH_3 as'	1476.1	9.9	$\text{S}_{13}(77.2) + \text{S}_{15}(11.6)$
$\nu\text{N}_{(3)}\text{-N}_{(4)}$	1461.4	58.5	$\text{S}_5(79.0)$
δCH_3 as''	1445.6	33.8	$\text{S}_{14}(83.2)$
δCH_3 s	1413.0	6.0	$\text{S}_{12}(84.2)$
$\delta\text{NH}_{(12)}$	1343.4	15.0	$\text{S}_{17}(63.3)$
$\delta\text{N-H}_{(11)}$	1276.4	76.2	$\text{S}_{30}(41.6) + \text{S}_7(13.3) + \text{S}_{18}(12.0)$
$\nu\text{N}_{(1)}\text{-N}_{(2)}$	1243.1	1.3	$\text{S}_8(23.1) + \text{S}_3(20.2) + \text{S}_{20}(20.2) + \text{S}_{15}(15.2)$
$\gamma\text{CH}_3'$	1221.5	45.6	$\text{S}_{15}(21.9) + \text{S}_3(20.1) + \text{S}_4(19.7) + \text{S}_{17}(19.3)$
$\gamma\text{CH}_3''$	1115.1	40.1	$\text{S}_{16}(84.2)$
$\delta\text{ring 2}$	1058.9	143.1	$\text{S}_{20}(16.2) + \text{S}_{30}(42.5) + \text{S}_6(10.4) + \text{S}_4(10.2)$
$\nu\text{N}_{(2)}\text{-N}_{(3)}$	999.7	53.9	$\text{S}_4(18.5) + \text{S}_{15}(35.0) + \text{S}_8(26.7)$
$\nu\text{N}_{(1)}\text{-C}_{(5)}$	968.4	16.2	$\text{S}_7(45.0) + \text{S}_{19}(14.9) + \text{S}_8(11.8)$
$\nu\text{N}_{(4)}\text{-C}_{(5)}$	891.4	17.7	$\text{S}_6(37.8) + \text{S}_4(25.4)$
$\tau\text{NH}_{(11)}$	792.4	40.4	$\text{S}_{29}(37.0) + \text{S}_{23}(20.1) + \text{S}_6(10.4)$
$\delta\text{ring 1}$	779.1	48.7	$\text{S}_{19}(12.5) + \text{S}_{29}(24.3) + \text{S}_6(16.0) + \text{S}_{20}(9.9)$
$\gamma\text{ring 1}$	746.8	36.4	$\text{S}_{23}(28.9) + \text{S}_{29}(29.4) + \text{S}_{22}(13.6) + \text{S}_{25}(11.2)$
$\nu\text{N-C(H}_3)$	672.3	64.2	$\text{S}_3(26.7) + \text{S}_8(15.3) + \text{S}_{22}(14.6) + \text{S}_{24}(12.3) + \text{S}_{20}(10.0)$
$\tau\text{ring 1}$	582.7	132.8	$\text{S}_{24}(39.3) + \text{S}_{19}(20.5) + \text{S}_{22}(14.9) + \text{S}_3(10.0)$
$\gamma\text{N-H}_{(12)}$	516.5	40.8	$\text{S}_{22}(30.1) + \text{S}_{24}(30.2) + \text{S}_{23}(21.8)$
$\omega\text{C-(NH}_{(11)})$	472.1	8.3	$\text{S}_{18}(61.2) + \text{S}_{27}(23.8)$
$\omega\text{N-(CH}_3)$	315.7	13.4	$\text{S}_{27}(45.6) + \text{S}_{18}(14.4) + \text{S}_{26}(14.1)$
$\tau\text{ring 2}$	256.5	25.2	$\text{S}_{25}(28.4) + \text{S}_{26}(33.9) + \text{S}_{27}(14.8)$
τCH_3	188.1	2.5	$\text{S}_{21}(89.7) + \text{S}_{25}(13.5)$
$\gamma\text{ring 2}$	130.0	9.3	$\text{S}_{26}(54.9) + \text{S}_{25}(29.1)$

^a Frequencies in cm^{-1} , calculated intensities in km mol^{-1} . ν , bond stretching, δ , bending, γ rocking, τ torsion, s, symmetric, as, antisymmetric. See Table S4 for definition of coordinates. Numbering of the atoms in the tetrazole ring follows that used for 2MTA

^b Only PED values greater than 9.5 % are given.

Table S9. DFT(B3LYP)/6-311++G(d,p) calculated frequencies and intensities, and normal coordinate analysis for 2-methyl-3*H*-tetrazol-2-ium-5-aminide (A).^a

Approximate Description	Calculated frequency	Intensity	PED ^b
$\nu\text{N-H}_{(12)}$	3524.0	133.0	$\text{S}_2(99.6)$
$\nu\text{N-H}_{(11)}$	3456.3	12.2	$\text{S}_{28}(99.8)$
νCH_3 as'	3077.8	2.5	$\text{S}_{10}(63.3) + \text{S}_{11}(36.2)$
νCH_3 as''	3059.7	5.2	$\text{S}_{11}(61.6) + \text{S}_{10}(36.8)$
νCH_3 s	2984.3	26.5	$\text{S}_9(97.7)$
$\nu\text{C-N}_{(H_{(11)})}$	1647.2	726.6	$\text{S}_1(76.9) + \text{S}_{19}(12.4)$
δCH_3 as'	1483.6	11.0	$\text{S}_{13}(59.3) + \text{S}_{15}(13.8) + \text{S}_{17}(11.9)$
$\delta\text{NH}_{(12)}$	1474.6	19.2	$\text{S}_{17}(30.2) + \text{S}_{13}(17.2) + \text{S}_{12}(16.2) + \text{S}_4(12.8)$
δCH_3 as''	1439.0	14.4	$\text{S}_{14}(87.2) + \text{S}_{16}(10.5)$
δCH_3 s	1413.3	12.5	$\text{S}_{12}(80.9) + \text{S}_{17}(10.3)$
$\nu\text{N}_{(1)}\text{-N}_{(2)}$	1368.1	17.3	$\text{S}_8(40.5) + \text{S}_5(22.9)$
$\nu\text{N}_{(2)}\text{-N}_{(3)}$	1330.1	2.4	$\text{S}_4(21.0) + \text{S}_5(19.4) + \text{S}_3(17.0)$
$\nu\text{N}_{(3)}\text{-N}_{(4)}$	1231.7	218.1	$\text{S}_5(26.3) + \text{S}_{17}(33.1) + \text{S}_{20}(12.5) + \text{S}_{30}(10.2)$
$\delta\text{N-H}_{(11)}$	1207.0	55.0	$\text{S}_{30}(44.5) + \text{S}_{20}(18.1)$
$\gamma\text{CH}_3''$	1109.2	9.9	$\text{S}_{16}(81.6) + \text{S}_{14}(9.9)$
$\delta\text{ring 2}$	1060.2	54.8	$\text{S}_{20}(30.1) + \text{S}_4(23.7) + \text{S}_{30}(17.8)$
$\gamma\text{CH}_3'$	1039.0	68.6	$\text{S}_{15}(44.9) + \text{S}_8(20.4) + \text{S}_4(9.7)$
$\nu\text{N}_{(1)}\text{-C}_{(5)}$	925.4	16.3	$\text{S}_7(55.7) + \text{S}_6(13.8)$
$\nu\text{N}_{(4)}\text{-C}_{(5)}$	904.7	104.2	$\text{S}_6(54.3) + \text{S}_7(17.8) + \text{S}_{19}(15.6)$
$\delta\text{ring 1}$	785.8	3.8	$\text{S}_{19}(47.0) + \text{S}_3(11.7) + \text{S}_{20}(11.3) + \text{S}_6(11.2) + \text{S}_1(11.6)$
$\gamma\text{ring 1}$	695.2	40.5	$\text{S}_{23}(63.3) + \text{S}_{29}(21.1) + \text{S}_{25}(14.6)$
$\tau\text{NH}_{(11)}$	663.6	68.8	$\text{S}_{29}(72.4) + \text{S}_{23}(20.6)$
$\nu\text{N-C}_{(H_3)}$	634.3	18.0	$\text{S}_3(36.3) + \text{S}_{19}(20.5) + \text{S}_{20}(15.8)$
$\tau\text{ring 1}$	576.8	21.7	$\text{S}_{24}(75.9) + \text{S}_{22}(21.3)$
$\omega\text{C-N}_{(H_{(11)})}$	483.2	21.1	$\text{S}_{18}(61.0) + \text{S}_{27}(23.2)$
$\gamma\text{N-H}_{(12)}$	358.6	59.2	$\text{S}_{22}(66.2) + \text{S}_{24}(37.1)$
$\omega\text{N-C}_{(H_3)}$	294.5	7.6	$\text{S}_{27}(56.3) + \text{S}_{18}(16.9)$
$\tau\text{ring 2}$	246.5	14.7	$\text{S}_{25}(55.6) + \text{S}_{26}(35.4) + \text{S}_{23}(10.3)$
$\gamma\text{ring 2}$	146.0	1.6	$\text{S}_{26}(49.3) + \text{S}_{25}(28.4) + \text{S}_{21}(21.7)$
τCH_3	84.7	1.5	$\text{S}_{21}(79.9) + \text{S}_{26}(31.2)$

^a Frequencies in cm^{-1} , calculated intensities in km mol^{-1} . ν , bond stretching, δ , bending, γ rocking, τ torsion, s, symmetric, as, antisymmetric. See Table S4 for definition of coordinates. Numbering of the atoms in the tetrazole ring follows that used for 2MTA

^b Only PED values greater than 9.5 % are given.

Table S10. DFT(B3LYP)/6-311++G(d,p) calculated frequencies and intensities, and normal coordinate analysis for 2-methyl-3*H*-tetrazol-2-ium-5-aminide (B).^a

Approximate Description	Calculated frequency	Intensity	PED ^b
$\nu\text{N-H}_{(12)}$	3514.9	111.8	$\text{S}_2(99.7)$
$\nu\text{N-H}_{(11)}$	3455.1	12.7	$\text{S}_{28}(99.8)$
νCH_3 as'	3081.8	1.9	$\text{S}_{10}(62.2) + \text{S}_{11}(37.4)$
νCH_3 as''	3065.5	4.1	$\text{S}_{11}(61.1) + \text{S}_{10}(38.0)$
νCH_3 s	2988.7	21.3	$\text{S}_9(98.4)$
$\nu\text{C-N}(\text{H}_{(11)})$	1647.0	724.3	$\text{S}_1(76.9) + \text{S}_{19}(12.5)$
δCH_3 as'	1486.7	3.8	$\text{S}_{13}(48.5) + \text{S}_8(14.0) + \text{S}_{15}(13.5) + \text{S}_{17}(12.9)$
$\delta\text{NH}_{(12)}$	1471.1	23.7	$\text{S}_{17}(22.0) + \text{S}_{13}(26.6) + \text{S}_{12}(15.4) + \text{S}_4(10.6)$
δCH_3 as''	1430.0	14.2	$\text{S}_{14}(87.0) + \text{S}_{16}(10.7)$
δCH_3 s	1413.1	11.7	$\text{S}_{12}(80.7)$
$\nu\text{N}_{(1)}\text{-N}_{(2)}$	1375.8	28.1	$\text{S}_8(35.7) + \text{S}_5(17.8) + \text{S}_4(14.0) + \text{S}_{13}(9.9) + \text{S}_{17}(9.5)$
$\nu\text{N}_{(2)}\text{-N}_{(3)}$	1327.0	26.1	$\text{S}_4(17.1) + \text{S}_5(17.2) + \text{S}_3(16.7)$
$\delta\text{N-H}_{(11)}$	1221.3	55.2	$\text{S}_{30}(37.2) + \text{S}_{17}(26.0) + \text{S}_5(10.3)$
$\nu\text{N}_{(3)}\text{-N}_{(4)}$	1185.7	132.8	$\text{S}_5(26.0) + \text{S}_{20}(29.9) + \text{S}_{30}(16.6)$
$\gamma\text{CH}_3''$	1110.4	6.5	$\text{S}_{16}(78.7) + \text{S}_{14}(9.8)$
$\delta\text{ring 2}$	1057.3	170.1	$\text{S}_{20}(21.1) + \text{S}_{30}(23.8) + \text{S}_8(17.7) + \text{S}_5(13.2) + \text{S}_4(10.5)$
$\gamma\text{CH}_3'$	1049.0	23.6	$\text{S}_{15}(49.3) + \text{S}_4(23.1)$
$\nu\text{N}_{(1)}\text{-C}_{(5)}$	937.0	48.2	$\text{S}_7(60.1) + \text{S}_{30}(10.5)$
$\nu\text{N}_{(4)}\text{-C}_{(5)}$	906.5	53.2	$\text{S}_6(62.3) + \text{S}_{19}(16.4) + \text{S}_7(9.8)$
$\delta\text{ring 1}$	780.3	6.7	$\text{S}_{19}(46.2) + \text{S}_{20}(12.1) + \text{S}_1(12.0) + \text{S}_6(11.9) + \text{S}_3(10.9)$
$\gamma\text{ring 1}$	696.4	27.7	$\text{S}_{23}(83.2) + \text{S}_{25}(13.5)$
$\tau\text{NH}_{(11)}$	667.6	32.6	$\text{S}_{29}(92.3)$
$\nu\text{N-C}(\text{H}_3)$	633.2	7.6	$\text{S}_3(37.4) + \text{S}_{19}(21.4) + \text{S}_{20}(15.3)$
$\tau\text{ring 1}$	569.3	57.1	$\text{S}_{24}(86.1) + \text{S}_{22}(11.4)$
$\omega\text{C-N}(\text{H}_{(11)})$	485.6	19.8	$\text{S}_{18}(61.4) + \text{S}_{27}(23.1)$
$\gamma\text{N-H}_{(12)}$	331.4	50.1	$\text{S}_{22}(55.0) + \text{S}_{27}(25.9) + \text{S}_{24}(18.9)$
$\omega\text{N-C}(\text{H}_3)$	285.9	51.9	$\text{S}_{27}(36.5) + \text{S}_{22}(28.6) + \text{S}_{18}(15.1)$
$\tau\text{ring 2}$	253.9	10.5	$\text{S}_{25}(50.2) + \text{S}_{26}(42.5)$
$\gamma\text{ring 2}$	150.6	3.3	$\text{S}_{26}(59.7) + \text{S}_{25}(34.7)$
τCH_3	82.7	1.1	$\text{S}_{21}(95.3) + \text{S}_{26}(11.1)$

^a Frequencies in cm^{-1} , calculated intensities in km mol^{-1} . ν , bond stretching, δ , bending, γ rocking, τ torsion, s, symmetric, as, antisymmetric. See Table S4 for definition of coordinates. Numbering of the atoms in the tetrazole ring follows that used for 2MTA

^b Only PED values greater than 9.5 % are given.