Equilibrium structures of 3-, 4-, 5-, 6-, and 7-membered unsaturated N-containing heterocycles

Supplementary Material

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Table S1. Extrapolation of the structure of 1-azirine to infinite basis set (rotational constants in MHz, distances in Å, and angles in degrees).

	A	*B*	*C*	C_2-C_3	N_1-C_3	$N_1C_2C_3$	C_2-H	N_1C_2H	C_3-H	C_2C_3H	HC_3C_2N
X_0 exp [a]	35615.599	22224.024	15064.613								
g [b]	–0.236	–0.186	0.031								
X_e-X_0	182.716	227.652	153.620								
X_e(T) [c]	35671.816	22368.221	15154.903	1.4496	1.5517	49.3682	1.0786	139.0780	1.0815	120.4361	99.3114
X_e(Q) [d]	35811.878	22474.859	15227.078	1.4476	1.5455	49.4142	1.0776	139.0622	1.0809	120.4187	99.3945
X_0(T) [e]	35489.100	22140.569	15001.283								
X_0(Q) [e]	35629.162	22247.207	15073.458								
r_e extrapol. [f]											
from A_0				1.4477	1.5459	49.411	1.0777	139.063	1.0809	120.420	99.389
ΔA+5%				1.4476	1.5455	49.414	1.0776	139.062	1.0809	120.419	99.395
from B_0				1.4480	1.5467	49.405	1.0778	139.065	1.0810	120.422	99.378
ΔB+5%				1.4478	1.5461	49.410	1.0777	139.064	1.0809	120.420	99.387
from C_0				1.4479	1.5463	49.408	1.0778	139.064	1.0809	120.421	99.384
ΔC+5%				1.4476	1.5457	49.413	1.0777	139.063	1.0809	120.419	99.393
mean				1.4479	1.5463	49.408	1.0778	139.064	1.0809	120.421	99.384

[a] Ref. 37.
[b] Diagonal elements of the *g*-tensor.
[c] Calculated from the CCSD(T)/wCVTZ_AE structure.
[d] Calculated from the CCSD(T)/wCVQZ_AE structure.
[e] $X_0 = X_e$ + rovibrational correction calculated with the B3LYP/6-311+G(3df,2pd) force field.
[f] See text.

Table S2. Ground-state rotational constants,[a] rovibrational corrections,[b] semiexperimental equilibrium rotational constants, and residuals of the fits for aziridine (MHz).

	c-C_2H_4NH	*c*-C_2H_4ND	*c*-$CHDNHCH_2$ *trans*	*c*-$CHDNHCH_2$ *cis*	*c*-$C_2H_4{}^{15}NH$	*c*-$^{13}CH_2NHCH_2$	*c*-$C_2H_4{}^{15}ND$	*c*-CD_2NHCH_2
φ[c]	0.0	177.1	17.4	16.5	0.3	8.7	177.5	20.6
A_0	22736.12	20678.35	21832.15	21775.24	22046.37	22600.73	20658.03	20883.91
B_0	21192.38	20583.08	19088.17	19097.61	21186.75	20684.72	20051.67	17299.26
C_0	13383.07	12796.97	12653.83	12689.57	13142.74	13132.66	12596.36	12116.01
A_e-A_0	260.14	214.34	249.31	246.22	247.92	257.17	213.77	234.61
B_e-B_0	220.89	225.06	187.79	191.14	220.64	213.08	215.92	165.65
C_e-C_0	168.15	156.15	151.16	154.52	163.89	163.64	152.65	142.20
A_e	22996.79	20893.12	22081.94	22021.94	22294.79	22858.42	20872.23	21118.96
B_e	21413.00	20807.88	19275.74	19288.54	21407.12	20897.55	20267.35	17464.74
C_e	13550.82	12952.75	12804.64	12843.73	13306.25	13295.92	12748.66	12257.88
ΔA[d]	–0.008	0.597	0.119	0.032	0.133	–0.032	0.126	0.107
ΔB[d]	–0.422	–0.490	–0.050	0.035	–0.441	–0.094	0.007	0.293
ΔC[d]	–0.095	0.170	–0.020	–0.075	–0.030	0.019	0.177	–0.089

[a] Ref. 43.
[b] From a MP2/VTZ cubic force field.
[c] Angle of rotation of the principal axis system upon isotopic substitution (in degrees).
[d] Residuals of the least-squares fit.

Table S3. Ground-state rotational constants, rovibrational corrections,[a] semiexperimental equilibrium rotational constants, residuals of the fit, equilibrium inertial defect Δ_e (uÅ^2), and angle of rotation φ of the principal axis system upon isotopic substitution (degree) for pyrrole (MHz).

	Parent	^{15}N	$^{13}C_2$	$^{13}C_3$	N-D	2-D	3-D
φ	0	0	a/b [b]	24.1	0	a/b [b]	32.4
A_0	9130.632	9131.090	9021.879	9099.129	9130.770	9018.390	9089.060
B_0	9001.363	8807.260	8892.736	8803.137	8340.830	8361.840	8272.450
C_0	4532.110	4482.470	4477.737	4473.678	4358.660	4338.300	4330.200
A_e-A_0	74.582	74.238	73.602	73.992	74.816	74.277	74.499
B_e-B_0	74.034	72.653	72.332	71.856	63.405	64.742	64.531
C_e-C_0	38.174	37.725	37.488	37.464	35.053	35.494	35.513
A_e	9205.663	9205.772	9095.915	9173.554	9206.036	9093.151	9163.979
B_e	9075.715	8880.213	8965.378	8875.289	8404.472	8426.875	8337.203
C_e	4570.096	4519.988	4515.039	4510.961	4393.544	4373.605	4365.549
Δ_e	0.0004	0.0011	0.0012	0.0004	-0.0010	0.0018	-0.0005
ΔA [d]	–0.095	0.015	0.030	-0.022	0.285	0.017	-0.010
ΔB [d]	–0.014	0.009	0.007	0.020	-0.025	0.017	-0.003
ΔC [d]	–0.038	–0.034	–0.038	–0.018	0.092	–0.062	0.016

[a] From a MP2(AE)/wCVTZ cubic force field.
[b] Switching of the axes *a* and *b*.
[c] Ground state constants of the parent species from Ref. 47.
[d] Residuals of the least-squares fit.

Table S4. Ground state rotational constants, rovibrational corrections,[a] semiexperimental equilibrium rotational constants, residuals of the fit, equilibrium inertial defect Δ_e (uÅ^2), and angle of rotation φ of the principal axis system upon isotopic substitution (degree) for pyrazole (MHz).

	Parent	N_1-D	3-D	4-D	5-D	$^{15}N_1$	$^{15}N_2$	$^{13}C_3$	$^{13}C_4$	$^{13}C_5$
φ	0	58.6	68.9	a/b [b]	36.5	a/b [b]	3.2	44.6	18.1	21.5
A_0	9618.770	9455.230	9435.783	9566.176	9537.304	9488.641	9618.304	9457.566	9582.358	9571.674
B_0	9412.535	8859.733	8774.190	8617.847	8677.868	9339.851	9180.010	9340.099	9193.394	9223.004
C_0	4755.853	4572.847	4545.189	4532.324	4542.381	4705.424	4695.610	4697.835	4690.511	4695.634
A_e-A_0	78.418	81.054	77.298	81.474	75.831	81.197	77.791	75.230	80.055	75.824
B_e-B_0	79.703	65.764	70.934	66.561	71.890	75.122	77.420	79.869	75.078	79.168
C_e-C_0	41.431	37.997	38.714	38.448	38.618	40.925	40.683	40.662	40.617	40.657
A_e	9697.604	9536.935	9513.701	9648.161	9613.613	9570.392	9696.509	9533.327	9662.884	9647.927
B_e	9492.919	8925.885	8845.526	8684.907	8750.287	9415.506	9258.078	9420.518	9269.072	9302.812
C_e	4797.119	4610.691	4583.751	4570.622	4580.849	4746.187	4736.131	4738.335	4730.967	4736.130
Δ_e	–0.0007	–0.0010	–0.0006	–0.0002	–0.0005	–0.0006	–0.0004	–0.0009	–0.0006	–0.0004
ΔA [c]	–0.154	0.012	0.098	0.035	–0.012	0.153	–0.059	0.239	0.117	–0.008
ΔB [c]	0.021	–0.053	–0.056	–0.018	–0.025	–0.189	–0.216	–0.212	–0.018	0.125
ΔC [c]	0.002	0.030	0.031	0.011	0.011	0.018	–0.051	0.048	0.049	–0.083

[a] From a B3LYP/6-311+G(3df,2pd)cubic force field.
[b] Switching of the axes *a* and *b*.
[c] Residuals of the least-squares fit.

Table S5. Ground-state rotational constants, rovibrational corrections,[a] semiexperimental equilibrium rotational constants, residuals of the fit, equilibrium inertial defect Δ_e (uÅ^2), and angle of rotation φ of the principal axis system upon isotopic substitution (degree) for imidazole (MHz).

	N	1-D	2-D	4-D	5-D	$^{15}N_1$	$^{15}N_3$	$^{13}C_2$	$^{13}C_4$	$^{13}C_5$	1,2-D_2
φ	0	19.3	a/b [b]	48.9	a/b [b]	10.1	4.1	15	21.2	a/b [b]	43.1
A_0	9725.311	9668.890	9388.986	9486.430	9586.963	9695.266	9721.525	9522.309	9573.910	9632.174	8941.102
B_0	9374.000	8699.544	8896.778	8778.552	8684.712	9188.161	9135.763	9354.011	9285.998	9225.520	8631.198
C_0	4771.919	4578.381	4566.964	4558.162	4555.633	4716.175	4708.476	4717.458	4712.612	4711.003	4390.939
A_e-A_0	76.961	76.801	71.182	74.678	73.964	76.812	76.428	73.658	75.837	74.678	68.526
B_e-B_0	71.526	61.014	68.102	64.573	64.695	69.896	69.305	72.053	69.825	70.929	60.421
C_e-C_0	38.796	35.492	36.328	36.219	36.040	38.300	38.050	38.116	38.073	38.068	33.384
A_e	9802.771	9746.184	9460.633	9561.582	9661.412	9772.573	9798.451	9596.444	9650.230	9707.341	9010.049
B_e	9446.064	8761.021	8965.364	8843.597	8749.868	9258.573	9205.578	9426.599	9356.351	9296.970	8692.075
C_e	4810.556	4613.727	4603.146	4594.237	4591.528	4754.321	4746.371	4755.419	4750.530	4748.917	4424.189
Δ_e	0.0000	–0.0009	0.0006	0.0013	0.0002	–0.0001	0.0003	–0.0008	–0.0005	–0.0012	–0.0022
ΔA [c]	–0.029	–0.230	–0.040	0.124	0.025	0.009	0.052	–0.085	–0.088	–0.579	–0.199
ΔB [c]	–0.126	0.002	0.006	0.006	0.001	–0.001	0.046	0.042	0.095	1.657	–0.002
ΔC [c]	–0.040	–0.015	–0.033	–0.025	–0.003	0.007	0.012	0.027	0.024	0.349	0.037

[a] From a B3LYP/6-311+G(3df,2pd)cubic force field.
[b] Switching of the axes *a* and *b*.
[c] Residuals of the least-squares fit.

Table S6. Ground-state rotational constants, rovibrational corrections,[a] semiexperimental equilibrium rotational constants, residuals of the fit, equilibrium inertial defect Δ_e (uÅ^2), and angle of rotation φ of the principal axis system upon isotopic substitution (degree) for pyridine (MHz).

	Parent	2-D	3-D	4-D	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$	^{15}N	D_5	$^{13}C_4$,^{15}N
φ	0.0	40.3	43.4	0.0	15.4	16.7	0.0	0.0	a/b [b]	0.0
A_0	6039.244	5900.883	5889.192	6038.996	5963.154	5956.596	6039.486	6039.483	5080.247	6039.644
B_0	5804.914	5558.521	5555.052	5420.072	5758.923	5756.020	5676.059	5680.395	4979.008	5553.923
C_0	2959.210	2861.714	2858.031	2855.822	2928.965	2926.631	2925.401	2926.545	2514.239	2892.642
A_e-A_0	45.306	42.042	41.597	45.612	43.957	43.859	45.088	45.144	33.507	44.978
B_e-B_0	38.599	38.599	38.398	35.018	38.616	38.652	37.508	37.410	34.542	36.300
C_e-C_0	21.857	20.956	20.807	20.771	21.531	21.516	21.480	21.468	17.541	21.091
A_e	6084.805	5943.180	5931.044	6084.871	6007.368	6000.713	6084.835	6084.895	5113.973	6084.883
B_e	5843.834	5597.418	5593.747	5455.370	5797.847	5794.980	5713.871	5718.116	5013.816	5590.520
C_e	2980.998	2882.607	2878.775	2876.530	2950.432	2948.083	2946.816	2947.948	2531.725	2913.669
Δ_e	–0.0031	–0.0029	–0.0028	–0.0033	–0.0034	–0.0033	–0.0032	–0.0026	–0.0020	–0.0031
ΔA [c]	–0.090	–0.215	–0.208	–0.024	–0.150	–0.208	–0.061	0.000	–0.057	–0.013
ΔB [c]	–0.135	0.020	0.018	–0.061	–0.023	0.032	–0.057	–0.069	–0.019	–0.071
ΔC [c]	–0.002	0.002	0.001	0.032	0.016	0.015	0.026	0.026	0.006	0.029

[a] From a B3LYP/6-311+G(3df,2pd)cubic force field.
[b] Switching of the axes *a* and *b*.
[c] Residuals of the least-squares fit.

Table S7. Ground-state rotational constants, rovibrational corrections,[a] semiexperimental equilibrium rotational constants, residuals of the fit, equilibrium inertial defect Δ_e (uÅ^2), and angle of rotation φ of the principal axis system upon isotopic substitution (degree) for pyrimidine (MHz).

	Parent	$^{13}C_2$	$^{13}C_4$	$^{13}C_5$	^{15}N
φ	--	0.0	12.2	0.0	36.1
A_0	6276.828	6152.684	6256.102	6132.820	6253.962
B_0	6067.166	6067.554	5957.231	6067.375	5954.158
C_0	3084.449	3054.270	3050.846	3049.330	3049.541
A_e-A_0	45.013	43.923	44.448	43.744	44.546
B_e-B_0	40.763	40.400	39.939	40.566	39.840
C_e-C_0	22.343	21.989	21.974	21.987	21.969
A_e	6322.186	6197.030	6300.961	6176.891	6298.821
B_e	6108.334	6108.219	5997.443	6108.292	5994.361
C_e	3106.741	3076.157	3072.718	3071.216	3071.409
Δ_e	–0.0016	–0.0003	0.0005	–0.0009	0.0001
ΔA [b]	–0.029	0.006	0.040	0.009	–0.043
ΔB [b]	0.047	–0.068	0.008	0.005	0.008
ΔC [b]	0.036	–0.011	0.001	0.019	–0.010

[a] From a B3LYP/6-311+G(3df,2pd)cubic force field.
[b] Residuals of the least-squares fit.

Table S8. Ground-state rotational constants, rovibrational corrections,[a] semiexperimental equilibrium rotational constants, residuals of the fit, equilibrium inertial defect Δ_e (uÅ^2), and angle of rotation φ of the principal axis system upon isotopic substitution (degree) for uracil (MHz).

	Parent	$^{15}N_1$	$^{15}N_3$	$^{15}N_1{}^{15}N_3$	$^{15}N_1{}^{15}N_3{}^{13}C_2$	$^{15}N_1{}^{15}N_3{}^{13}C_4$	$^{15}N_1{}^{15}N_3{}^{13}C_5$	$^{15}N_1{}^{15}N_3{}^{13}C_6$	$^{15}N_1{}^{15}N_3{}^{18}O_7$	$^{15}N_1{}^{15}N_3{}^{18}O_8$
φ	--	0.56	0.02	0.59	0.77	0.77	0.07	0.60	1.43	2.52
A_0	3883.870	3854.029	3857.093	3827.192	3823.197	3824.729	3789.660	3741.917	3773.296	3781.208
B_0	2023.731	2012.584	2023.799	2012.640	2001.260	1999.401	2001.112	2012.664	1935.759	1929.547
C_0	1330.927	1322.605	1327.807	1319.462	1314.090	1313.468	1310.043	1309.182	1279.833	1278.020
A_e-A_0	32.176	31.807	32.199	31.843	31.609	31.667	31.279	30.790	31.134	31.168
B_e-B_0	12.721	12.666	12.621	12.582	12.431	12.400	12.520	12.580	11.974	11.973
C_e-C_0	8.847	8.783	8.806	8.753	8.659	8.651	8.669	8.664	8.404	8.403
A_e	3916.161	3885.950	3889.406	3859.147	3854.918	3856.508	3821.048	3772.814	3804.539	3812.485
B_e	2036.505	2025.302	2036.473	2025.274	2013.743	2011.853	2013.684	2025.296	1947.781	1941.568
C_e	1339.783	1331.397	1336.622	1328.223	1322.757	1322.128	1318.721	1317.855	1288.246	1286.431
Δ_e	0.00000	–0.00013	0.00036	0.00015	–0.00003	0.00028	0.00004	–0.00023	0.00028	0.00019
ΔA [b]	0.006	0.008	0.028	0.043	–0.012	0.001	–0.028	–0.030	–0.009	–0.007
ΔB [b]	0.012	–0.004	–0.011	–0.009	–0.002	–0.002	0.003	0.016	–0.001	0.001
ΔC [b]	0.006	0.000	–0.003	0.001	–0.002	–0.002	–0.002	0.004	–0.002	–0.001

[a] From a B3LYP/6-311+G(3df,2pd) cubic force field, followed by a scaling, see text.
[b] Residuals of the least-squares fit with 21 predicates, see text.