Термодинамика и структурные параметры катионов при азотировании $R^+ + N_2 = R\text{-}N_2^+$

№	Reaction	ΔE, kJ/mol	ΔG, kJ/mol	LUMO, Eh		Ring Deviation *, Å		Angle C-N-N	Distance, Å	
				R^+	$R\text{-}N_2^+$	R^+	$R\text{-}N_2^+$		C-N	N-N
1	$CH_3^+(S) + N_2 = CH_3\text{-}N_2^+(S)$	-199.59	-142.34	-0.486590	-0.326390			180	1.4558	1.1029
2	$CH_3^+(T) + N_2 = CH_3\text{-}N_2^+(S)$	-539.27	-461.53	-0.544280	-0.326390			180	1.4558	1.1029
3	$C_2H_5^+(S) + N_2 = C_2H_5\text{-}N_2^+(S)$	-53.88	3.44	-0.324030	-0.309530			178	1.4893	1.1032
4	$C_2H_5^+(T) + N_2 = C_2H_5\text{-}N_2^+(S)$	-407.19	-319.55	-0.496720	-0.309530			178	1.4893	1.1032
5	$1\text{-}CH_3\text{-}C_2H_4^+(S) + N_2 = 1\text{-}CH_3\text{-}C_2H_4\text{-}N_2^+(S)$	9.98	70.31	-0.347960	-0.293210			178	1.5442	1.1033
6	$1\text{-}CH_3\text{-}C_2H_4^+(T) + N_2 = 1\text{-}CH_3\text{-}C_2H_4\text{-}N_2^+(S)$	-359.08	-273.87	-0.466640	-0.293210			178	1.5442	1.1033
7	$1,1\text{-}(CH_3)_2\text{-}C_2H_3^+(S) + N_2 = 1,2\text{-}(CH_3)_2\text{-}C_2H_3\text{-}N_2^+(S)$	-7.79	19.95	-0.321560	-0.314080			**Break C-NN bond****		
8	$1,1\text{-}(CH_3)_2\text{-}C_2H_3^+(T) + N_2 = 1,2\text{-}(CH_3)_2\text{-}C_2H_3\text{-}N_2^+(S)$	-387.82	-346.28	-0.428030	-0.314080			**Break C-NN bond****		
9	$Pyridine\text{-}2^+(S) + N_2 = Pyridine\text{-}2\text{-}N_2^+(S)$	-53.71	1.37	-0.343690	-0.312160	0.0005	0.0003	179	1.4249	1.1090
10	$Pyridine\text{-}2^+(T) + N_2 = Pyridine\text{-}2\text{-}N_2^+(S)$	-225.00	-160.50	-0.430750	-0.312160	0.0012	0.0003	179	1.4249	1.1090
11	$Pyridine\text{-}3^+(S) + N_2 = Pyridine\text{-}3\text{-}N_2^+(S)$	-116.91	-58.51	-0.341510	-0.314260	0.0011	0.0007	178	1.3788	1.1145
12	$Pyridine\text{-}3^+(T) + N_2 = Pyridine\text{-}3\text{-}N_2^+(S)$	-219.46	-156.54	-0.416460	-0.314260	0.2607	0.0007	178	1.3788	1.1145
13	$Pyridine\text{-}4^+(S) + N_2 = Pyridine\text{-}4\text{-}N_2^+(S)$	-108.65	-45.36	-0.368060	-0.324880	0.0005	0.0000	180	1.3961	1.1108
14	$Pyridine\text{-}4^+(T) + N_2 = Pyridine\text{-}4\text{-}N_2^+(S)$	-194.84	-132.27	-0.411220	-0.324880	0.0002	0.0000	180	1.3961	1.1108
15	$Pyrazine\text{-}2^+(S) + N_2 = Pyrazine\text{-}2\text{-}N_2^+(S)$	-39.04	14.35	-0.355910	-0.328560	0.0007	0.0004	178	1.4177	1.1098
16	$Pyrazine\text{-}2^+(T) + N_2 = Pyrazine\text{-}2\text{-}N_2^+(S)$	-213.58	-152.55	-0.435720	-0.328560	0.2523	0.0004	178	1.4177	1.1098
17	$Pyrimidine\text{-}2^+(S) + N_2 = Pyrimidine\text{-}2\text{-}N_2^+(S)$	-54.97	-1.77	-0.342040	-0.322520	0.0003	0.0003	180	1.4750	1.1050
18	$Pyrimidine\text{-}2^+(T) + N_2 = Pyrimidine\text{-}2\text{-}N_2^+(S)$	-189.81	-132.64	-0.413720	-0.322520	0.0019	0.0003	180	1.4750	1.1050
19	$Pyrimidine\text{-}4^+(S) + N_2 = Pyrimidine\text{-}4\text{-}N_2^+(S)$	-26.71	27.02	-0.360100	-0.335000	0.0026	0.0001	178	1.4490	1.1064

№	Reaction	ΔE, kJ/mol	ΔG, kJ/mol	LUMO, Eh		Ring Deviation *, Å		Angle C-N-N	Distance, Å	
				R^+	$R\text{-}N_2^+$	R^+	$R\text{-}N_2^+$		C-N	N-N
20	Pyrimidine-4^+(T) + N_2 = Pyrimidine-4-N_2^+(S)	-203.93	-145.46	-0.434950	-0.335000	0.0000	0.0001	178	1.4490	1.1064
21	Pyrimidine-5^+(S) + N_2 = Pyrimidine-5-N_2^+(S)	-141.60	-79.98	-0.381390	-0.329610	0.0004	0.0003	180	1.3745	1.1148
22	Pyrimidine-5^+(T) + N_2 = Pyrimidine-5-N_2^+(S)	-176.32	-117.09	-0.413310	-0.329610	0.0002	0.0003	180	1.3745	1.1148
23	1,2,3-Triazine-4^+(S) + N_2 = 1,2,3-Triazine-4-N_2^+(S)	179.45	238.99	-0.365020	-0.354470	**Break****	0.0005	176	1.4319	1.1073
24	1,2,3-Triazine-4^+(T) + N_2 = 1,2,3-Triazine-4-N_2^+(S)	-125.09	-72.87	-0.422920	-0.354470	0.0000	0.0005	176	1.4319	1.1073
25	1,2,3-Triazine-5^+(S) + N_2 = 1,2,3-Triazine-5-N_2^+(S)	-55.78	-3.28	-0.393150	-0.360700	0.0029	0.0002	180	1.3883	1.1125
26	1,2,3-Triazine-5^+(T) + N_2 = 1,2,3-Triazine-5-N_2^+(S)	-155.51	-94.75	-0.439120	-0.360700	0.0001	0.0002	180	1.3883	1.1125
27	1,2,4-Triazine-3^+(S) + N_2 = 1,2,4-Triazine-3-N_2^+(S)	-74.18	-19.36	-0.368740	-0.342270	0.0001	0.0006	178	1.4584	1.1051
28	1,2,4-Triazine-3^+(T) + N_2 = 1,2,4-Triazine-3-N_2^+(S)	-132.43	-78.42	-0.414170	-0.342270	0.0009	0.0006	178	1.4584	1.1051
29	1,2,4-Triazine-5^+(S) + N_2 = 1,2,4-Triazine-5-N_2^+(S)	15.25	64.31	-0.369260	-0.355380	0.0003	0.0010	176	1.4461	1.1075
30	1,2,4-Triazine-5^+(T) + N_2 = 1,2,4-Triazine-5-N_2^+(S)	-136.61	-83.51	-0.440980	-0.355380	0.0012	0.0010	176	1.4461	1.1075
31	1,2,4-Triazine-6^+(S) + N_2 = 1,2,4-Triazine-6-N_2^+(S)	-62.76	-9.77	-0.389840	-0.348200	0.0015	0.0003	180	1.4036	1.1102
32	1,2,4-Triazine-6^+(T) + N_2 = 1,2,4-Triazine-6-N_2^+(S)	-128.97	-73.90	-0.420710	-0.348200	0.0016	0.0003	180	1.4036	1.1102
33	1,3,5-Triazine-2^+(S) + N_2 = 1,3,5-Triazine-2-N_2^+(S)	-35.85	15.91	-0.365090	-0.342070	0.0001	0.0005	180	1.5140	1.1031
34	1,3,5-Triazine-2^+(T) + N_2 = 1,3,5-Triazine-2-N_2^+(S)	-196.47	-140.56	-0.440040	-0.342070	0.0003	0.0005	180	1.5140	1.1031
35	N-O-Pyridine-2^+(S) + N_2 = N-O-Pyridine-2-N_2^+(S)	-215.96	-154.44	-0.387160	-0.317800	0.4951	0.0003	179	1.3630	1.1160
36	N-O-Pyridine-2^+(T) + N_2 = N-O-Pyridine-2-N_2^+(S)	-124.11	-65.02	-0.385440	-0.317800	0.0012	0.0003	179	1.3630	1.1160
37	N-O-Pyridine-3^+(S) + N_2 = N-O-Pyridine-3-N_2^+(S)	-142.18	-81.23	-0.377790	-0.322550	0.2439	0.0017	180	1.3877	1.1126
38	N-O-Pyridine-3^+(T) + N_2 = N-O-Pyridine-3-N_2^+(S)	-92.34	-34.08	-0.388810	-0.322550	0.0009	0.0017	180	1.3877	1.1126

№	Reaction	ΔE, kJ/mol	ΔG, kJ/mol	LUMO, Eh		Ring Deviation *, Å		Angle C-N-N	Distance, Å	
				R^+	$R\text{-}N_2^+$	R^+	$R\text{-}N_2^+$		C-N	N-N
39	N-O-Pyridine-4$^+$(S) + N_2 = N-O-Pyridine-4-N_2^+(S)	-201.93	-139.29	-0.382040	-0.311690	0.4161	0.0001	180	1.3635	1.1193
40	N-O-Pyridine-4$^+$(T) + N_2 = N-O-Pyridine-4-N_2^+(S)	-123.27	-63.77	-0.381640	-0.311690	0.0000	0.0001	180	1.3635	1.1193
41	Ph^+(S) + N_2 = Ph-N_2^+(S)	-146.51	-82.64	-0.353450	-0.300120	0.0000	0.0000	180	1.3832	1.1138
42	Ph^+(T) + N_2 = Ph-N_2^+(S)	-226.20	-162.01	-0.410940	-0.300120	0.0000	0.0000	180	1.3832	1.1138
43	4-NO_2-Ph^+(S) + N_2 = 4-NO_2-Ph-N_2^+(S)	-158.28	-95.37	-0.375810	-0.324090	0.0002	0.0001	180	1.3887	1.1126
44	4-NO_2-Ph^+(T) + N_2 = 4-NO_2-Ph-N_2^+(S)	-226.48	-159.35	-0.422680	-0.324090	0.0037	0.0001	180	1.3887	1.1126
45	4-CH_3O-Ph^+(S) + N_2 = 4-CH_3O-Ph-N_2^+(S)	-180.96	-115.57	-0.341610	-0.274560	0.2471	0.0003	180	1.3636	1.1193
46	4-CH_3O-Ph^+(T) + N_2 = 4-CH_3O-Ph-N_2^+(S)	-165.01	-104.32	-0.361220	-0.274560	0.0000	0.0003	180	1.3636	1.1193
47	Pyrrole-2$^+$(S) + N_2 = Pyrrole-2-N_2^+(S)	-223.46	-162.43	-0.376060	-0.291020	0.5921	0.0015	178	1.3369	1.1243
48	Pyrrole-2$^+$(T) + N_2 = Pyrrole-2-N_2^+(S)	-164.23	-103.72	-0.377920	-0.291020	0.0002	0.0015	178	1.3369	1.1243
49	Pyrrole-3$^+$(S) + N_2 = Pyrrole-3-N_2^+(S)	-254.26	-194.22	-0.368370	-0.282580	0.4555	0.0006	178	1.3494	1.1179
50	Pyrrole-3$^+$(T) + N_2 = Pyrrole-3-N_2^+(S)	-198.93	-136.85	-0.382350	-0.282580	0.0006	0.0006	178	1.3494	1.1179
51	Pyrazole-3$^+$(S) + N_2 = Pyrazole-3-N_2^+(S)	-250.11	-186.62	-0.409800	-0.308180	0.0012	0.0003	179	1.3684	1.1129
52	Pyrazole-3$^+$(T) + N_2 = Pyrazole-3-N_2^+(S)	-258.28	-194.97	-0.429440	-0.308180	0.0017	0.0003	179	1.3684	1.1129
53	Pyrazole-4$^+$(S) + N_2 = Pyrazole-4-N_2^+(S)	-268.87	-208.11	-0.397020	-0.300790	0.0041	0.0010	178	1.3493	1.1171
54	Pyrazole-4$^+$(T) + N_2 = Pyrazole-4-N_2^+(S)	-246.44	-184.73	-0.419130	-0.300790	0.0002	0.0010	178	1.3493	1.1171
55	Pyrazole-5$^+$(S) + N_2 = Pyrazole-5-N_2^+(S)	-253.80	-191.53	-0.410820	-0.320440	0.4261	0.0010	180	1.3486	1.1191
56	Pyrazole-5$^+$(T) + N_2 = Pyrazole-5-N_2^+(S)	-202.39	-137.36	-0.424260	-0.320440	0.0005	0.0010	180	1.3486	1.1191
57	1,3,5-$(CH_3)_3$-Pyrazole-4$^+$(S) + N_2 = 1,3,5-$(CH_3)_3$-Pyrazole-4-N_2^+(S)	-236.83	-176.05	-0.342360	-0.269760	0.2741	0.0001	178	1.3370	1.1219
58	1,3,5-$(CH_3)_3$-Pyrazole-4$^+$(T) + N_2 = 1,3,5-$(CH_3)_3$-Pyrazole-4-N_2^+(S)	-204.97	-144.06	-0.361090	-0.269760	0.0001	0.0001	178	1.3370	1.1219

№	Reaction	ΔE, kJ/mol	ΔG, kJ/mol	LUMO, Eh		Ring Deviation *, Å		Angle C-N-N	Distance, Å	
				R^+	$R\text{-}N_2^+$	R^+	$R\text{-}N_2^+$		C-N	N-N
63	Imidazole-2^+(S) + N_2 = Imidazole-2-N_2^+(S)	-217.32	-156.79	-0.402920	-0.312960	0.5496	0.0019	178	1.3516	1.1200
64	Imidazole-2^+(T) + N_2 = Imidazole-2-N_2^+(S)	-167.17	-107.33	-0.406700	-0.312960	0.0003	0.0019	178	1.3516	1.1200
65	Imidazole-4^+(S) + N_2 = Imidazole-4-N_2^+(S)	-243.12	-183.65	-0.406090	-0.299360	0.0023	0.0003	179	1.3619	1.1151
66	Imidazole-4^+(T) + N_2 = Imidazole-4-N_2^+(S)	-203.90	-142.69	-0.403750	-0.299360	0.0012	0.0003	179	1.3619	1.1151
67	Imidazole-5^+(S) + N_2 = Imidazole-5-N_2^+(S)	-244.64	-182.75	-0.389650	-0.308350	0.0298	0.0003	177	1.3387	1.1225
68	Imidazole-5^+(T) + N_2 = Imidazole-5-N_2^+(S)	-179.01	-118.29	-0.403480	-0.308350	0.0007	0.0003	177	1.3387	1.1225
69	1H-1,2,3-Triazole-4^+(S) + N_2 = 1H-1,2,3-Triazole-4-N_2^+(S)	-275.37	-215.43	-0.429960	-0.321380	0.0003	0.0013	177	1.3588	1.1143
70	1H-1,2,3-Triazole-4^+(T) + N_2 = 1H-1,2,3-Triazole-4-N_2^+(S)	-256.57	-191.78	-0.443080	-0.321380	0.0010	0.0013	177	1.3588	1.1143
71	1H-1,2,3-Triazole-5^+(S) + N_2 = 1H-1,2,3-Triazole-5-N_2^+(S)	-265.78	-204.79	-0.431980	-0.340350	0.0004	0.0013	178	1.3472	1.1186
72	1H-1,2,3-Triazole-5^+(T) + N_2 = 1H-1,2,3-Triazole-5-N_2^+(S)	-77.73	4.70	-0.401420	-0.340350	**Break****	0.0013	178	1.3472	1.1186
73	1H-1,2,4-Triazole-3^+(S) + N_2 = 1H-1,2,4-Triazole-3-N_2^+(S)	-254.35	-194.67	-0.425940	-0.328560	0.0002	0.0004	179	1.3825	1.1101
74	1H-1,2,4-Triazole-3^+(T) + N_2 = 1H-1,2,4-Triazole-3-N_2^+(S)	-267.82	-205.32	-0.451180	-0.328560	0.0013	0.0004	179	1.3825	1.1101
75	1H-1,2,4-Triazole-5^+(S) + N_2 = 1H-1,2,4-Triazole-5-N_2^+(S)	-249.79	-186.49	-0.440850	-0.344420	0.2600	0.0003	179	1.3654	1.1151
76	1H-1,2,4-Triazole-5^+(T) + N_2 = 1H-1,2,4-Triazole-5-N_2^+(S)	-213.99	-153.40	-0.450940	-0.344420	0.0004	0.0003	179	1.3654	1.1151
77	2H-1,2,3-Triazole-4^+(S) + N_2 = 2H-1,2,3-Triazole-4-N_2^+(S)	-280.14	-218.91	-0.434110	-0.327940	0.0001	0.0011	178	1.3651	1.1130
78	2H-1,2,3-Triazole-4^+(T) + N_2 = 2H-1,2,3-Triazole-4-N_2^+(S)	-281.59	-216.71	-0.461460	-0.327940	0.0006	0.0011	178	1.3651	1.1130
79	4H-1,2,4-Triazole-3^+(S) + N_2 = 4H-1,2,4-Triazole-3-N_2^+(S)	-227.98	-167.20	-0.415010	-0.337800	0.0004	0.0021	175	1.3551	1.1173
80	4H-1,2,4-Triazole-3^+(T) + N_2 = 4H-1,2,4-Triazole-3-N_2^+(S)	-217.42	-153.30	-0.445670	-0.337800	0.0002	0.0021	175	1.3551	1.1173
81	Tetrazole-5^+(S) + N_2 = Tetrazole-5-N_2^+(S)	22.83	85.87	-0.365710	-0.368930	**Break****	0.0010	177	1.3642	1.1139
82	Tetrazole-5^+(T) + N_2 = Tetrazole-5-N_2^+(S)	-259.18	-194.27	-0.475980	-0.368930	0.0012	0.0010	177	1.3642	1.1139

№	Reaction	ΔE, kJ/mol	ΔG, kJ/mol	LUMO, Eh		Ring Deviation *, Å		Angle C-N-N	Distance, Å	
				R^+	$R\text{-}N_2^+$	R^+	$R\text{-}N_2^+$		C-N	N-N
83	Furan-2^+(S) + N_2 = Furan-2-N_2^+(S)	-251.67	-190.57	-0.401650	-0.312500	0.5993	0.0002	179	1.3428	1.1209
84	Furan-2^+(T) + N_2 = Furan-2-N_2^+(S)	-184.15	-123.40	-0.405900	-0.312500	0.0019	0.0002	179	1.3428	1.1209
85	Furan-3^+(S) + N_2 = Furan-3-N_2^+(S)	-269.85	-209.84	-0.404520	-0.308260	0.4382	0.0004	179	1.3556	1.1157
86	Furan-3^+(T) + N_2 = Furan-3-N_2^+(S)	-201.39	-140.11	-0.410180	-0.308260	0.0003	0.0004	179	1.3556	1.1157
87	Thiophene-2^+(S) + N_2 = Thiophene-2-N_2^+(S)	-226.28	-165.76	-0.371020	-0.304400	0.6611	0.0003	179	1.3457	1.1204
88	Thiophene-2^+(T) + N_2 = Thiophene-2-N_2^+(S)	-189.03	-128.11	-0.395210	-0.304400	0.0012	0.0003	179	1.3457	1.1204
89	Thiophene-3^+(S) + N_2 = Thiophene-3-N_2^+(S)	-196.71	-134.52	-0.367640	-0.300420	0.0000	0.0004	179	1.3654	1.1162
90	Thiophene-3^+(T) + N_2 = Thiophene-3-N_2^+(S)	-201.88	-139.89	-0.401770	-0.300420	0.0003	0.0004	179	1.3654	1.1162

* Ring Deviation - суммарное отклонение атомов от плоскости цикла (ангстрем); ** Break - разрыв цикла или связи C-NN;

1. Азотирование карбкатионов характеризуется уменьшением энергии Гиббса. Наблюдаются низкие значения энергии связывания для соединений пиридина и алифатических диазониевых катионов и тетразола. Для третбутилового катиона 1,2-$(CH_3)_2$-$C_2H_3^+$ при оптимизации геометрии связь C-N-N не образуется.
2. Угол связи C-N-N близок к 180° для всех диазониевых катионов.
3. В случаях нарушения плоскости цикла в исходных карбкатионах при азотировании происходит восстановление плоской структуры.
4. Образовавшиеся диазониевые катионы сохраняют отрицательные значения LUMO и характеризуются высокой энергией сродства к электрону (EA).
5. Для всех рассматриваемых катионов при азотировании происходит увеличение энергии LUMO (уменьшение сродства к электрону), вне зависимости от энергии связывания!!! (даже в случае положительных значений энергии Гиббса)