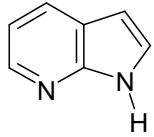
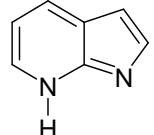
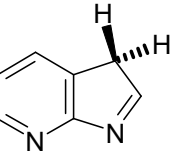
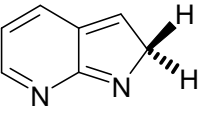
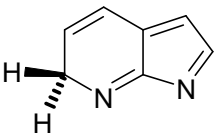
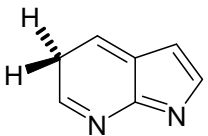
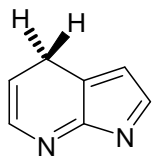
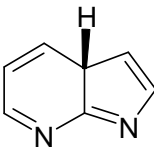
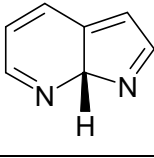


**UV-induced hydrogen-atom transfer and hydrogen-atom
detachment in monomeric 7-azaindole isolated
in Ar and n-H₂ matrices**

Maciej J. Nowak, Igor Reva, Hanna Rostkowska and Leszek Lapinski

Electronic Supplementary Information

Table S1 The relative energies of prototropic tautomers of 7-azaindole. The energies were calculated at the DFT(B3LYP)/6-311++G(d,p) level.

STRUCTURE	FORM	$\Delta E / \text{kJ}\cdot\text{mol}^{-1}$
	N1H	0.0
	N7H	52.1
	C3H	62.3
	C2H	145.7
	C6H	166.3
	C5H	167.5
	C4H	184.5
	C9H	203.0
	C8H	203.4

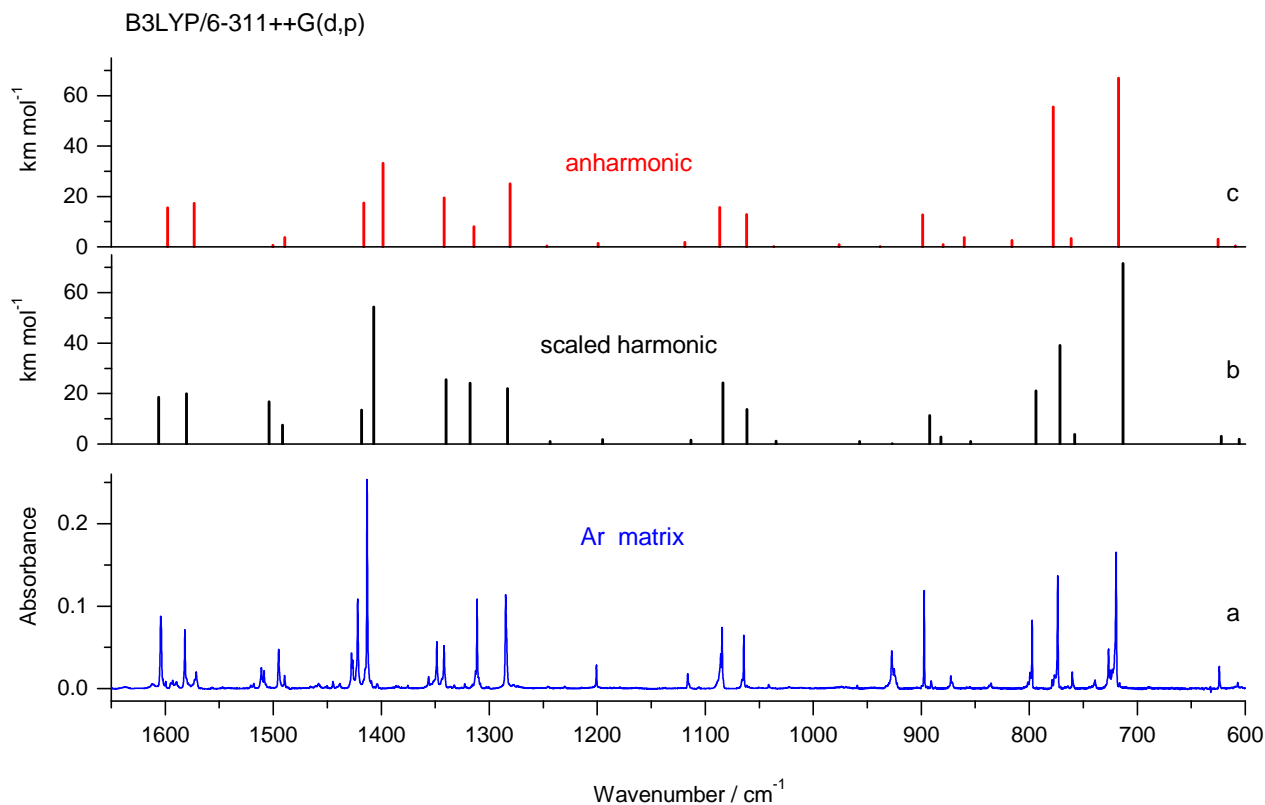


Figure S1. (a) Infrared spectrum of 7-azaindole monomers isolated in an Ar matrix, compared with the theoretical spectra calculated for the **N1H** isomer. Theoretical spectra were computed: (b) within harmonic approximation; (c) taking into account anharmonic effects, as defined in Gaussian 09, Revision D.01. The theoretical harmonic wavenumbers were scaled by a factor of 0.98. The calculations were carried out at the DFT(B3LYP)/6-311++G(d,p) level.

Table S2 Experimental wavenumbers (ν) and relative integrated intensities (I) of the bands in the spectra of 7-azaindole monomers isolated in Ar and n-H₂ matrices. The experimental spectra are compared with the theoretical spectrum [wavenumbers (ν) and absolute intensities (A)] calculated, at the DFT(B3LYP)/6-311++G(d,p) level, for the **N1H** tautomer of the compound. The theoretical harmonic wavenumbers were scaled by a single factor of 0.98. Integrated intensities of the experimental bands (I) were normalized in such a way that their sum (over all the experimental bands reported in the table) is equal to the sum of absolute intensities of the assigned theoretical bands.

Ar matrix		H ₂ matrix		DFT(B3LYP)/6-311++G(d,p) harmonic, scaled		DFT(B3LYP)/6-311++G(d,p) anharmonic.	
N1H				N1H		N1H	
ν	I	ν	I	ν	A	ν	A
cm ⁻¹	rel.	cm ⁻¹	rel.	cm ⁻¹	$\frac{km}{mol}$	cm ⁻¹	$\frac{km}{mol}$
3509/3505	99	3506	89	3590	89	3498	70
				3192	1	3121	4
				3172	2	3104	1
3100	4	3098	5	3128	18	3059	17
3071/3067	6	3066/3061	12	3106	11	3047	11
3035	6	3039	6	3092	12	3017	11
1604	17	1604	15	1607	19	1598	16
1582	11	1583/1581	15	1581	20	1573	17
1511/1508	8	1512/1509	9	1504	17	1500	1
1495	8	1495	5	1492	8	1489	4
1422	14	1423	20	1419	13	1416	17
1413	38	1414	30	1407	54	1398	33
1349/1341	22	1353/1345	16	1340	26	1342	19
1311	17	1311	14	1318	24	1314	8
1285	20	1284	25	1283	22	1281	25
				1244	1	1247	0.4
1201	2	1202	2	1195	2	1199	1
1116	2	1116	2	1114	1	1119	2
1086/1084	17	1088	14	1084	24	1087	15
1064	8	1065	5	1062	14	1062	12
1041	1	1036	0	1035	1	1037	0.1
959	1	963	1	958	1	976	1
927/925	17	946	18			962	21
				927	0.1	938	0.2
897	10	898	8	893	11	899	13
891	1	880	2	882	3	880	1
872	3	860	1	856	1	861	4
799/797	12	799	18	794	21	816	3
779/779/773	20	777	23	772	39	778	56
760	3	759	3	758	4	761	3
		744	4				
719	30	726	43	714	72	718	67
624	3	624	2	622	3	626	3
607	< 1			606	2	610	0.4
582	< 1	581	1	581	3	585	3
				550	0.5	556	1
458	26	467	26	460	51	475	54
425	8			422	9	426	9
417	15			416	21	424	15
				236	0.1	242	0.3
				215	15	218	14

2 γ N1-H overtone

γ N1-H

Table S3 Experimental wavenumbers (ν) and relative integrated intensities (I) of the bands in the spectrum of **N7H** tautomer generated upon UV ($\lambda > 270$ nm) irradiation of 7-azaindole monomers isolated in an Ar matrix. The experimental spectrum is compared with the theoretical spectrum [wavenumbers (ν) and absolute intensities (A)] calculated, at the DFT(B3LYP)/6-311++G(d,p) level, for the **N7H** tautomer. The theoretical harmonic wavenumbers were scaled by a single factor of 0.98. Integrated intensities of the experimental bands (I) were normalized in such a way that their sum (over all the experimental bands reported in the table) is equal to the sum of absolute intensities of the assigned theoretical bands.

Ar matrix		DFT(B3LYP)/ 6-311++G(d,p) harmonic, scaled		DFT(B3LYP)/ 6-311++G(d,p) anharmonic	
N7H		N7H		N7H	
ν	I	ν	A	ν	A
cm ⁻¹	rel.	cm ⁻¹	$\frac{km}{mol}$	cm ⁻¹	$\frac{km}{mol}$
3430/ <u>3427</u> /3423	148	3510	75	3426	60
		3175	7	3102	16
		3161	1	3089	1
		3140	10	3085	74
		3140	3	3085	68
		3107	9	3025	12
1617	31	1617	35	1607	15
1589	78	1589	56	1581	46
1517/1513	30	1509	51	1506	32
		1463	0.4	1466	4
		1450	9	1447	4
1401	50	1410	25	1402	13
1367/ <u>1366</u>	43	1365	24	1364	27
1315	107	1313	125	1309	74
1272	9	1272	10	1273	5
1216	11	1214	10	1216	7
		1192	1	1199	1
1129/1126	60	1136	62	1135	42
1092	18	1092	6	1096	8
		1051	1	1054	1
1029	23	1026	21	1030	14
		938	2	985	0.03
		900	2	937	9
904	6	899	5	913	5
878	9	877	5	906	2
		873	10	878	9
		762	18	810	4
		747	0.07	775	69
		736	2	750	0.1
727	48	721	117	742	116
702	28	699	40.	733	73
		601	1	621	1
		592	2	606	1
		558	3	593	1
552	10	550	6	555	6
		419	7	425	6
		384	11	412	18
		245	9	253	8
		209	1	221	1

Table S4 Experimental wavenumbers (ν) and relative integrated intensities (I) of the bands in the spectra of **C3H** tautomer generated upon UV ($\lambda > 270$ nm) irradiation of 7-azaindole monomers isolated in Ar and n-H₂ matrices. The experimental spectra are compared with the theoretical spectrum [wavenumbers (ν) and absolute intensities (A)] calculated, at the DFT(B3LYP)/6-311++G(d,p) level, for the **C3H** tautomer. The theoretical harmonic wavenumbers were scaled by a single factor of 0.98. Integrated intensities of the experimental bands (I) were normalized in such a way that their sum (over all the experimental bands reported in the table) is equal to the sum of absolute intensities of the assigned theoretical bands.

Ar matrix		H ₂ matrix		DFT(B3LYP)/6-311++G(d,p) harmonic, scaled		DFT(B3LYP)/6-311++G(d,p) anharmonic	
C3H				C3H		C3H	
ν	I	ν	I	ν	A	ν	A
cm ⁻¹	rel.	cm ⁻¹	rel.	cm ⁻¹	$\frac{km}{mol}$	cm ⁻¹	$\frac{km}{mol}$
				3129	15	3049	15
				3103	9	3039	10
				3103	12	3019	14
				3091	15	2996	14
				2995	3	2895	4
				2967	6	2886	7
				1613	18	1608	14
				1581	5	1574	68
1562/1560	29	1562	29	1579	67	1570	31
				1467	1	1463	1
1401	45	1402	22	1404	24	1396	21
1389/1387	48	1389/1387	33	1386	52	1384	16
				1317	0.1	1313	4
1314	24	1314	18	1309	20	1305	6
1280	21	1281	30	1283	15	1278	11
1210	21	1213/1210	40	1217	24	1212	18
				1203	5	1202	5
				1153	1	1154	0.4
				1119	2	1116	1
1103	7	1102	9	1098	6	1102	6
				1042	1	1045	0
				971	0.2	991	4
967	2	968	3	966	2	976	1
		928	2	930	1	935	1
904	6	904	8	914	6	915	7
869	7	869	6	861	5	867	5
				855	1	860	0
811	63	813	61	809	51	814	33
				762	7	772	4
				746	1	757	3
				742	3	745	3
				618	0.1	629	0.2
				574	0.4	585	1
				546	1	551	1
				428	5	433	5
				416	0.06	423	0.01
				392	0.01	406	0.03
				212	7	218	7
				192	0.04	195	0.1

Table S5 Experimental wavenumbers (ν) and relative integrated intensities (I) of the bands in the spectra of 7-azaindoyl radical generated upon UV ($\lambda > 270$ nm) irradiation of 7-azaindole monomers isolated in Ar and n-H₂ matrices. The experimental spectra are compared with the theoretical spectrum [wavenumbers (ν) and absolute intensities (A)] calculated, at the DFT(B3LYP)/6-311++G(d,p) level, for the 7-azaindoyl radical. The theoretical wavenumbers were scaled by a single factor of 0.98. Integrated intensities of the experimental bands (I) were normalized in such a way that their sum (over all the experimental bands reported in the table) is equal to the sum of absolute intensities of the assigned theoretical bands.

Ar matrix		H ₂ matrix		DFT(B3LYP) /6-311++G(d,p)	
Radical				Radical	
ν	I	ν	I	ν	A
cm ⁻¹	rel.	cm ⁻¹	rel.	cm ⁻¹	$\frac{km}{mol}$
				3156	9
				3133	13
				3129	6
				3109	9
				3099	10
				1578	39
1556	82	1555	117	1563	87
				1471	3
				1450	1
1372	16	1372	6	1379	19
1325	27	1325	8	1331	20
1299	19	1299	22	1303	26
1247	23	1246	13	1253	13
				1215	6
				1184	4
1158	17	1157	11	1154	9
1090	14	1089	12	1088	9
				1037	1
				952	0.5
				946	4
				927	0.1
				887	5
				877	5
840	10	839	7	835	5
786	48	786	59	779	67
				756	7
				750	0.3
				713	1
				599	5
				553	2
				539	0.2
				490	0.2
				435	6
				403	0.02
				220	1
				201	6

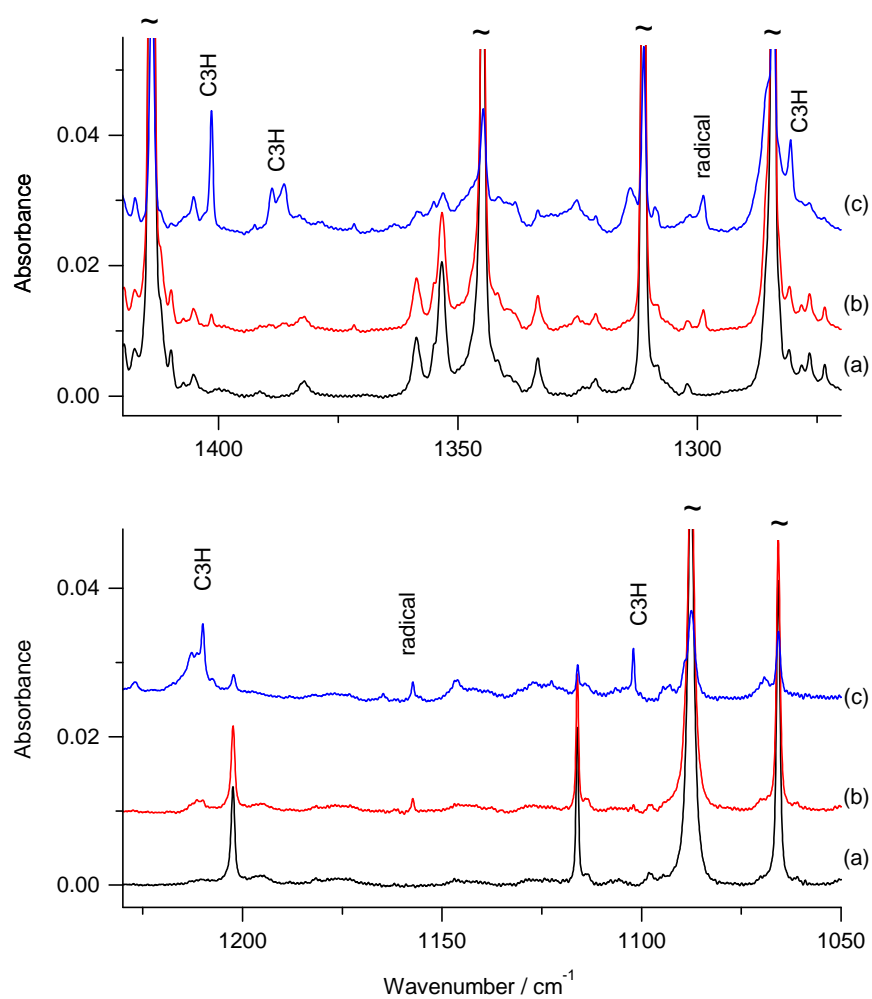


Figure S2. Fragments of the infrared spectra of 7-azaindole isolated in an n-H₂ matrix: (a) the spectrum recorded after deposition of the n-H₂ matrix and before any irradiation; (b) the spectrum recorded after 1 min. of UV ($\lambda > 270$ nm) irradiation; (c) the spectrum recorded after 31 min. of UV ($\lambda > 270$ nm) irradiation.