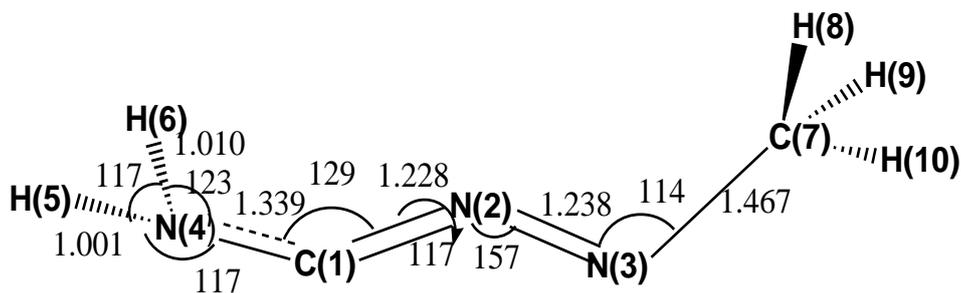


## Infrared-spectroscopic study of amino-substituted nitrilimines and their photochemical transformations in an argon matrix

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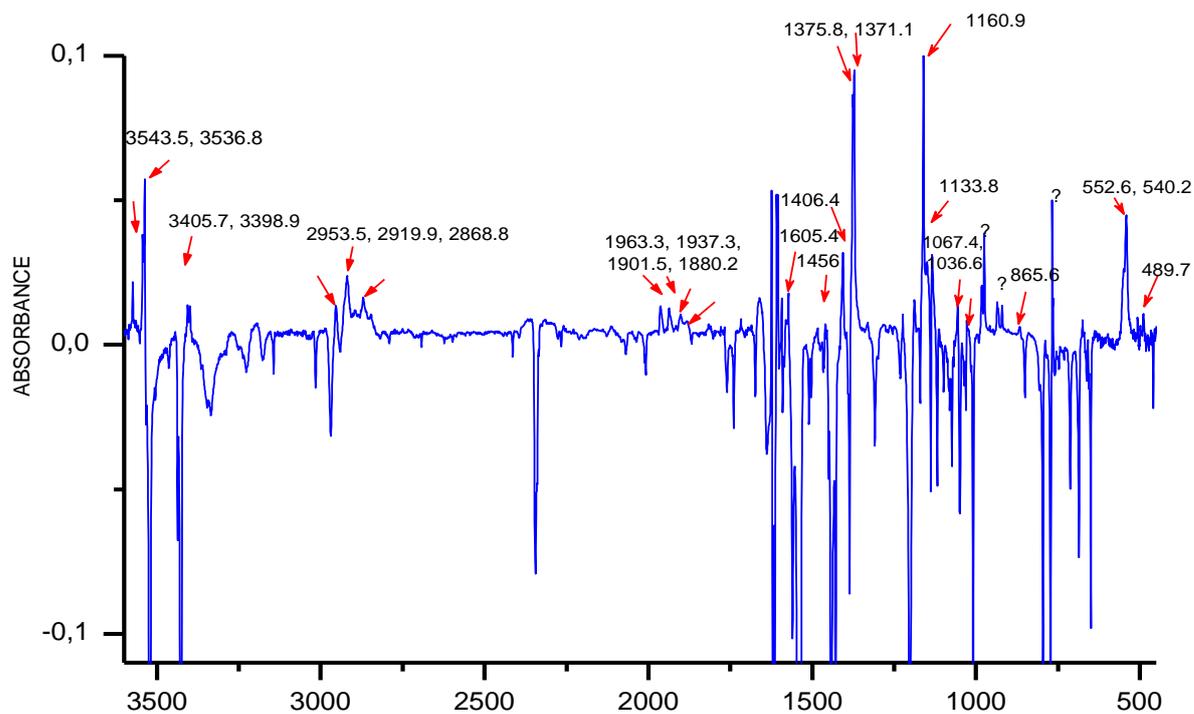
$E = -243.466173 \text{ h}$

$E_0 = -243.389167 \text{ h}$

**Figure S1** Structure of 3-amino-1-methylnitrileimine (**2**) calculated at the B3LYP/cc-pVTZ level (length of bonds (Å), bond angles (°) and dihedral bond angles (°)).

**Table S1.** Cartesian coordinates of the optimized structure of 3-amino-1-methylnitrileimine (**2**), calculated at the B3LYP/cc-pVTZ level of theory.

N	Atom	X	Y	Z
1	C	0.119410	0.208470	0.155602
2	N	0.550886	0.187951	1.305332
3	N	1.359965	-0.019522	2.219446
4	N	-0.232113	1.263038	-0.590619
5	H	-0.604900	1.108373	-1.506978
6	H	-0.013060	2.214747	-0.333866
7	C	0.743017	-0.186137	3.542198
8	H	-0.340650	-0.051025	3.525536
9	H	0.978882	-1.186278	3.912699
10	H	1.191868	0.531856	4.230859

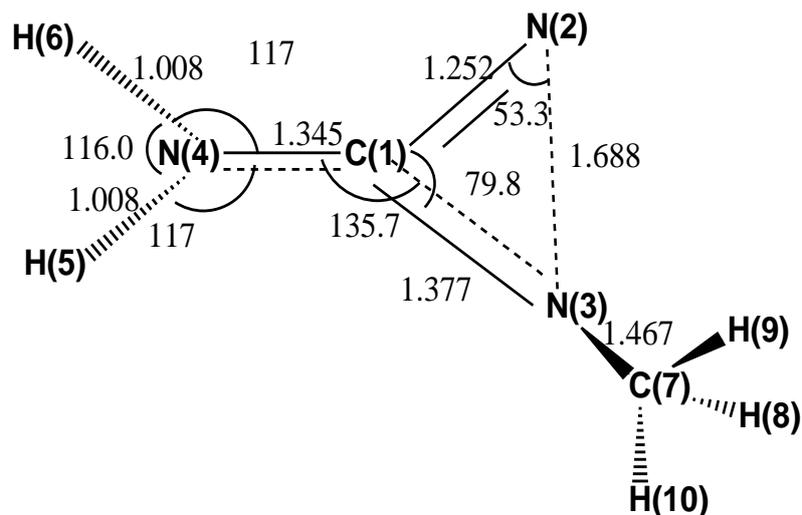


**Figure S2** IR difference spectrum between the spectrum of 5-amino-2-methyl-2H-tetrazole (**1**) in Ar matrix at 10 K and the spectrum after its UV photolysis ( $\lambda=254$  nm) in the gas phase. Peaks with positive absorptions are due to photolysis products, negative – to tetrazole **1**. Bands, denoted with arrows, are assigned to nitrilimine - 3-amino-1-methylnitrileimine (**2**).

**Table S2** Assignment for the Infrared bands of 3-amino-1-methylnitrileimine (**2**) observed in Ar matrices, and corresponding calculated (B3LYP/cc-pVTZ) frequencies ( $\text{cm}^{-1}$ ) with their IR Intensities ( $\text{km/mol}$ ).

Approximate Assignment <sup>a</sup>	Experimental Frequencies $\nu^b$	Calculated Frequencies		
		Scaled <sup>c</sup>	Unscaled	Intensity
$\nu\text{NH}_2$ as	3543.5 m, 3536.8 m	3593	3701	78
$\nu\text{NH}_2$ s	3405.7 w, 3398.9 w	3421	3523	0
$\nu\text{CH}_3$ as	2953.5 m	2995	3085	24
$\nu\text{CH}_3$ as	2919.9 m	2981	3071	22
$\nu\text{CH}_3$ s	2868.8 m	2918	3006	59
$\nu\text{C}(1)\text{N}(2)\text{N}(3)$ as, $\nu\text{C}(1)\text{N}(4)$	1880.2 w	1898	1955	108
$\delta\text{NH}_2$ s	1605.4 m	1577	1649	35
$\delta\text{CH}_3$ as	1456.0 m	1458	1500	70
$\delta\text{CH}_3$ as	1449.1 w	1431	1475	5
$\nu\text{C}(1)\text{N}(2)\text{N}(3)$ s, $\nu\text{C}(1)\text{N}(4)$ , $\delta\text{CH}_3$ s	1406.4 s	1395	1460	70
$\delta\text{CH}_3$ s	1375.8 vs, 1371.1 vs	1375	1416	63
$r\text{CH}_3$ as	1160.9 m	1138	1173	22
$r\text{NH}_2$ as	1133.8 sh.m	1124	1158	107
$r\text{CH}_3$ as	1067.4 w	1065	1097	3
$\nu\text{C}(1)\text{N}(4)$ , $\nu\text{C}(7)\text{N}(3)$	1036.6 w	1030	1061	14
$\nu\text{C}(7)\text{N}(3)$	865.6 vw	848	874	4
$\tau\text{NH}_2$	552.6 m	594	611	33
$\delta\text{N}(2)\text{C}(1)\text{N}(4)$	540.2 vs	545	561	59
$\delta\text{C}(1)\text{N}(2)\text{N}(3)$	489.7 w	490	505	8

<sup>a</sup> $\nu$  – bond stretching,  $\delta$  – bending,  $r$  – rocking,  $\tau$  – torsion; s – symmetric, as – antisymmetric. <sup>b</sup>vs – very strong, s – strong, sh – shoulder, m – medium, w – weak, <sup>c</sup> scaling factor 0.9709 for B3LYP/cc-pVTZ (P. Sinha, S. E. Boesch, C. Gu, R. A. Wheeler, A. K. Wilson *J. Phys. Chem. A*, **2004**, *108* (42), pp 9213–9217).



$E = -243.465578 \text{ h}$

$E_0 = -243.387666 \text{ h}$

**Figure S3** Structure of 3-amino-1-methyl-1*H*-diazirene (**3**) calculated at the B3LYP/cc-pVTZ level of theory (length of bonds (Å), bond angles (°)).

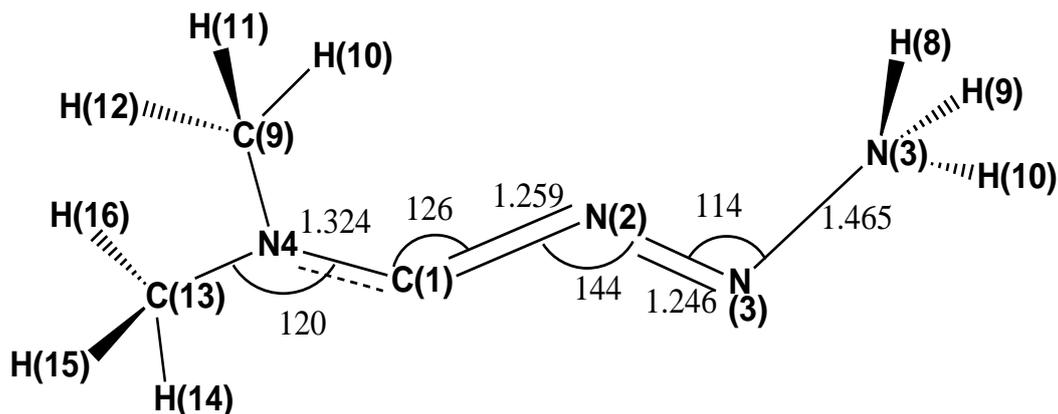
**Table S3** Cartesian coordinates of the optimized structure of 3-amino-1-methyl-1*H*-diazirene (**3**) calculated at the B3LYP/cc-pVTZ level of theory.

N	Atom	X	Y	Z
1	C	0.286702	0.704196	0.403057
2	N	0.212850	1.048048	1.604484
3	N	1.616900	0.652478	0.754004
4	N	-0.429166	0.431175	-0.702390
5	H	0.070753	0.437438	-1.576374
6	H	-1.380225	0.762378	-0.735040
7	C	2.104223	-0.679283	1.128647
8	H	1.303214	-1.360227	1.429366
9	H	2.634359	-1.103230	0.270852
10	H	2.814240	-0.576587	1.947678

**Table S4** Assignment for the infrared bands of 3-amino-1-methyl-1*H*-diazirene (**3**), observed in Ar matrices, and corresponding calculated (B3LYP/cc-pVTZ) frequencies (cm<sup>-1</sup>) with their IR intensities (km/mol).

Approximate Assignment <sup>a</sup>	Experimental Frequencies	Calculated Frequencies		
	$\nu^b$	Scaled <sup>c</sup>	Unscaled	Intensity
$\nu\text{NH}_2$ as	3564.7 w	3567	3674	45
$\nu\text{NH}_2$ s		3459	3563	35
$\nu\text{CH}_3$ as	2994.8 m	3011	3102	22
$\nu\text{CH}_3$ as	2950.6 m	2971	3061	23
$\nu\text{CH}_3$ s	2895.5 w	2912	3000	38
$\nu\text{N}(2)\text{C}(1)\text{N}(4)$ s	1821.4 sh. m, 1815.7 vs, 1810.8 vs	1825	1879	250
$\delta\text{NH}_2$	1584.3 m	1577	1625	39
$\delta\text{CH}_3$ as	1457.8 m	1458	1502	7
$\delta\text{CH}_3$ as	1434.8 w	1431	1475	5
$\delta\text{CH}_3$ s	1402 sh.w	1395	1438	2
$\nu\text{N}(2)\text{C}(1)\text{N}(4)$ s	1358.6 s	1345	1385	63
$r\text{CH}_3$ as		1134	1169	2
$r\text{CH}_3$ as		1096	1129	3
$r\text{NH}_2$ as	1013.5 w	1052	1083	4
$\nu\text{N}(4)\text{C}(7)$	976.8 m	1000	1030	6
$\nu\text{C}(1)\text{N}(4)\text{C}(7)$	836.9 w	825	850	12
$\delta\text{C}(1)\text{N}(3)\text{C}(7)$	658.8 w	657	677	15
$\delta\text{N}(2)\text{C}(1)\text{N}(3)$	511 b w	511	527	11

<sup>a</sup> $\nu$  – bond stretching,  $\delta$  – bending,  $r$  – rocking; s – symmetric, as – antisymmetric, <sup>b</sup>vs – very strong, s – strong, sh – shoulder, b-broad, m – medium, w – weak, <sup>c</sup>scaling factor 0.9709 (see Table S2)



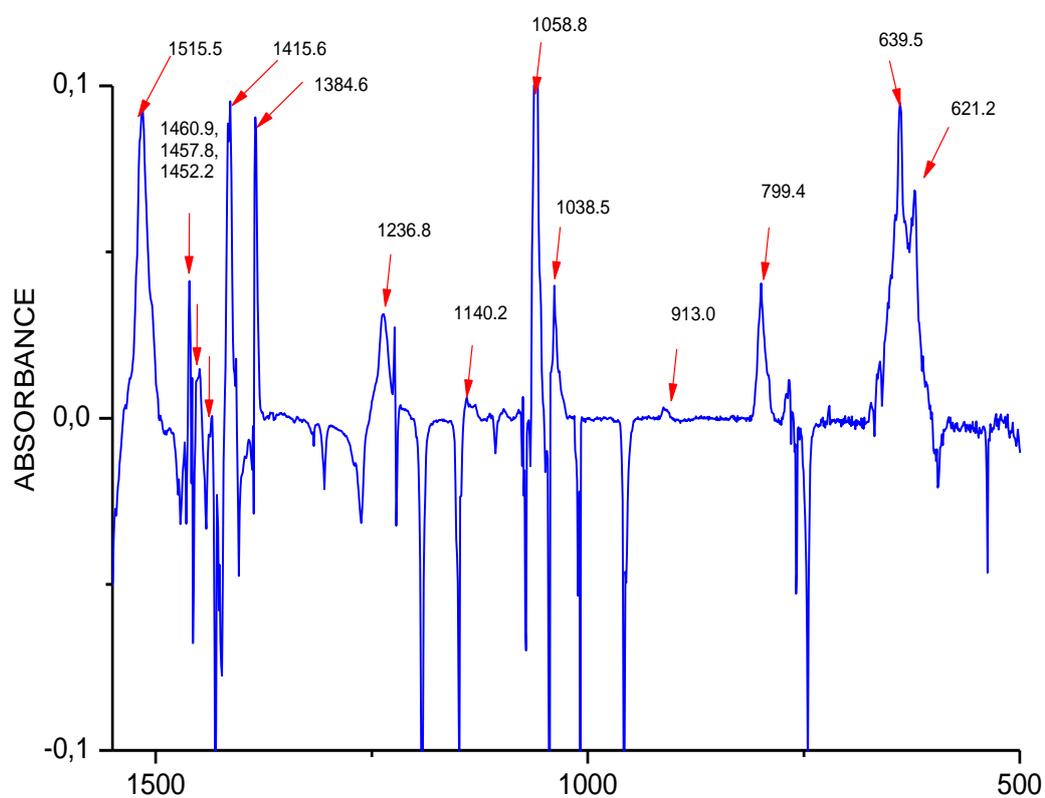
$$E = -322.108666 \text{ h}$$

$$E_0 = -321.975551 \text{ h}$$

**Figure S4** Structure of 3-(dimethyl)amino-1-methylnitrileimine (**12**) calculated at the B3LYP/cc-pVTZ level of theory (length of bonds (Å), bond angles (°) and dihedral bond angles (°)).

**Table S5** Cartesian coordinates of the optimized structure of 3-(dimethyl)amino-1-methylnitrileimine (**12**) calculated at the B3LYP/cc-pVTZ level of theory.

N	Atom	X	Y	Z
1	6	-0.053105	-0.069161	-0.045526
2	7	-0.149606	-0.091026	1.209253
3	7	0.494067	-0.024828	2.273692
4	7	-0.428799	0.915391	-0.847619
5	6	-0.267508	-0.464745	3.445774
6	1	-1.309728	-0.694192	3.212062
7	1	0.214925	-1.351442	3.865002
8	1	-0.222168	0.317826	4.205477
9	6	-0.860551	2.230549	-0.377244
10	1	-0.759848	2.282899	0.702532
11	1	-0.248114	3.016056	-0.825168
12	1	-1.903641	2.411241	-0.651678
13	6	-0.496594	0.702981	-2.284650
14	1	-1.526360	0.797150	-2.642615
15	1	0.115567	1.439639	-2.811227
16	1	-0.130811	-0.294160	-2.507745

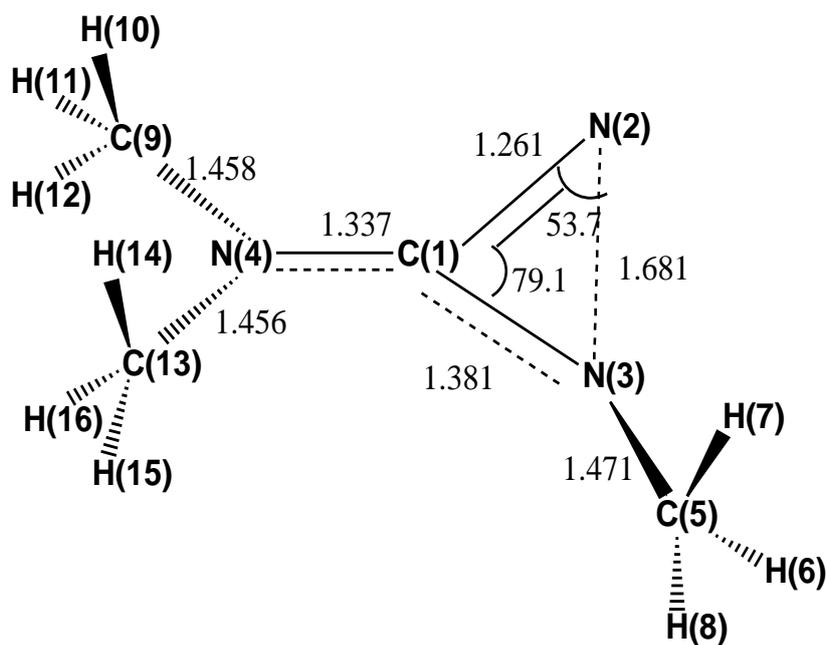


**Figure S5** Partial IR difference spectrum between the spectrum of 5-dimethylamino-2-methyl-2*H*-tetrazole (**11**) in Ar matrix at 10 K and the spectrum after its UV photolysis ( $\lambda=254$  nm) in the gas phase. Peaks with positive absorptions are due to photolysis products, negative – to tetrazole **11**. Bands, denoted with arrows, are assigned to nitrilimine - 3-(dimethyl)amino-1- methylnitrileimine (**12**).

**Table S6** Assignment for the infrared bands of 3-(dimethyl)amino-1-methylnitrileimine (**12**), observed in Ar matrices, and corresponding calculated (B3LYP/cc-pVTZ) frequencies ( $\text{cm}^{-1}$ ) with their IR intensities ( $\text{km/mol}$ ).

Approximate Assignment <sup>a</sup>	Experimental Frequencies	Calculated Frequencies		
	$\nu^b$	Scaled <sup>c</sup>	Unscaled	Intensity
$\nu(\text{CH}_3)_2$ as		3055	3147	5
$\nu(\text{CH}_3)_2$ as		3051	3143	4
$\nu\text{CH}_3$ as		2992	3082	25
$\nu\text{CH}_3$ as	2987.3 w	2974	3064	23
$\nu(\text{CH}_3)_2$ as	2954.3 m	2971	3061	21
$\nu(\text{CH}_3)_2$ as	2937.2 m	2960	3049	44
$\nu(\text{CH}_3)_2$ s	2902.3 w	2924	3013	72
$\nu(\text{CH}_3)_2$ s	2872 w	2916	3004	28
$\nu\text{CH}_3$ s	2854.6 w	2914	3002	109
$\nu\text{C}(1)\text{N}(2)\text{N}(3)$ as, $\nu\text{C}(1)\text{N}(4)$	1725 vw	1737	1789	86
$\nu\text{C}(1)\text{N}(4)$ , $\delta(\text{CH}_3)_2$ s	1515.5 vs	1518	1564	141
$\delta(\text{CH}_3)_2$ as	1460.9 sh. m	1457	1501	6
$\delta\text{CH}_3$ s, $\delta(\text{CH}_3)_2$ s	1457.8 m	1455	1499	50
$\delta(\text{CH}_3)_2$ as	1452.2 m	1448	1492	16
$\delta\text{CH}_3$ s, $\delta(\text{CH}_3)_2$ s	1448.3 m	1442	1485	3
$\delta(\text{CH}_3)_2$ as		1438	1482	0
$\delta\text{CH}_3$ as		1431	1474	4
$\delta(\text{CH}_3)_2$ s	1415.6 s	1408	1450	56
$\delta(\text{CH}_3)_2$ s	1405.6 m	1399	1441	5
$\delta\text{CH}_3$ s	1384.6 s	1377	1418	34
$\nu\text{C}(1)\text{N}(2)\text{N}(3)$ s	1236.8 m	1243	1281	22
$\nu\text{C}(9)\text{N}(4)\text{C}(13)$ as		1202	1239	14
$R(\text{CH}_3)_2$ s		1134	1168	2
$r\text{CH}_3$ s	1140.2 w	1122	1156	9
$R(\text{CH}_3)_2$ as		1083	1116	1
$r\text{CH}_3$ as	1065.4 w	1067	1099	1
$r\text{CH}_3$ as	1058.8 s	1046	1078	83
$r(\text{CH}_3)_2$ as	1038.5 m	1021	1052	16
$\nu\text{C}(3)\text{N}(7)$	913.0 w	891	918	4
$\nu\text{C}(9)\text{N}(4)\text{C}(13)$ s	799.4 m	786	809	23
$\delta\text{N}(2)\text{C}(1)\text{N}(4)$	639.5,vs, 621.2 s	623	642	173
$\delta\text{C}(1)\text{N}(2)\text{N}(3)$	470.4 m	470	484	11

<sup>a</sup> $\nu$  – bond stretching,  $\delta$  – bending,  $r$  – rocking; s – symmetric, as – antisymmetric. <sup>b</sup>vs – very strong, s – strong, sh – shoulder, m – medium, w – weak, vw – very weak <sup>c</sup>scaling factor 0.9709 (see Table S2)



**E = -322.108319 h**  
**E<sub>0</sub> = -321.974515 h**

**Figure S6** Structure of 3-(dimethyl)amino-1-methyl -1*H*-diazirine (**13**), calculated at the B3LYP/cc-pVTZ level of theory (length of bonds (Å), bond angles (°)).

**Table S7** Cartesian coordinates of the optimized structure of 3-(dimethyl)amino-1-methyl -1*H*-diazirine (**13**) calculated at the B3LYP/cc-pVTZ level of theory.

N	Atom	X	Y	Z
1	C	-0.001436	0.004879	0.011831
2	N	-0.007004	-0.029839	1.270040
3	N	1.350911	-0.008399	0.278192
4	N	-0.779293	0.031665	-1.070960
5	C	1.976104	-1.334484	0.222606
6	H	1.257531	-2.151900	0.332026
7	H	2.494174	-1.435408	-0.735803
8	H	2.719224	-1.405580	1.015445
9	C	-2.221768	0.102359	-0.911330
10	H	-2.602275	1.084872	-1.203989
11	H	-2.708370	-0.657175	-1.526269
12	H	-2.473377	-0.076420	0.131222
13	C	-0.210868	0.226369	-2.391797
14	H	-0.529917	1.182858	-2.815364
15	H	0.873485	0.228643	-2.318540
16	H	-0.522502	-0.572355	-3.068780

**Table S8** Assignment for the Infrared Bands of 3-(dimethyl)amino-1-methyl-1*H*-diazirine (**13**), observed in Ar matrices and corresponding calculated (B3LYP/cc-pVTZ) frequencies (cm<sup>-1</sup>), with their IR intensities.

Approximate Assignment <sup>a</sup>	Experimental Frequencies	Calculated Frequencies		
	$\nu^b$	Scaled <sup>c</sup>	Unscaled	Intensity
$\nu(\text{CH}_3)_2$ as		3043	3134	5
$\nu(\text{CH}_3)_2$ as		3039	3130	5
$\nu\text{CH}_3$ as		3008	3099	25
$\nu(\text{CH}_3)_2$ as		2975	3064	16
$\nu\text{CH}_3$ as		2967	3056	29
$\nu(\text{CH}_3)_2$ as		2965	3054	41
$\nu(\text{CH}_3)_2$ s	2924.8 m	2926	3014	75
$\nu(\text{CH}_3)_2$ s		2921	3009	36
$\nu\text{CH}_3$ s	2913.0 w	2908	2996	43
$\nu\text{N}(2)\text{C}(1)\text{N}(3)$ as	1810.8 vs	1804	1858	<b>431</b>
$\delta(\text{CH}_3)_2$ s		1488	1533	2
$\delta(\text{CH}_3)_2$ as	1466.6 w	1463	1507	17
$\delta\text{CH}_3$ s		1459	1503	6
$\delta(\text{CH}_3)_2$ s		1449	1493	16
$\delta\text{CH}_3, \delta(\text{CH}_3)_2$ as		1439	1483	0
$\delta\text{CH}_3$ as		1430	1473	7
$\delta\text{CH}_3$ as	1433.0 w	1427	1470	12
$\delta(\text{CH}_3)_2$ s		1409	1451	1
$\delta\text{CH}_3$ as		1396	1437	4
$\nu\text{N}(2)\text{C}(1)\text{N}(4)$ s	1377.8 s	1366	1407	52
$\nu\text{C}(1)\text{N}(3), \delta(\text{CH}_3)_2$ as	1281.2 s	1275	1313	41
$\nu\text{C}(9)\text{N}(4)\text{C}(13)$ as, $\nu\text{C}(1)\text{N}(3)$		1204	1240	6
$r(\text{CH}_3)_2$ s	1140.1 w	1141	1175	4
$r\text{CH}_3$ as	1129.8 w	1117	1151	6
$R(\text{CH}_3)_2$ as		1097	1129	1
$r\text{CH}_3$ as		1084	1117	2
$r(\text{CH}_3)_2$ as	1062.0 m	1055	1086	7
$r\text{CH}_3$ s	1030.8 m	1014	1044	50
$\nu\text{C}(5)\text{N}(3)$	934.6 w	911	939	9
$\nu\text{C}(9)\text{N}(4)\text{C}(13)$ s		727	749	2

<sup>a</sup> $\nu$  – bond stretching,  $\delta$  – bending,  $r$ – rocking; s – symmetric, as – antisymmetric. <sup>b</sup>vs – very strong, s – strong, m – medium, w – weak, <sup>c</sup>scaling factor 0.9709 (see Table S2)

## Experimental details

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a 300 and 75.5 MHz NMR spectrometer «Bruker AVANCE II 300» for solutions in  $\text{CDCl}_3$  containing 0.05% of  $\text{Me}_4\text{Si}$  as an internal standard or in  $\text{CD}_3\text{CN}$ . Mass spectra were obtained using a «Finnigan MAT INCOS-50» (EI, 70 eV, direct inlet probe). TLC analysis was performed on Silica gel 60 («Merck») chromatographic plates; spots were visualized under the iodine vapor. For preparative chromatography, Silica gel 60 (0.040–0.063 mm, «Merck») on column or plate with a ratio of substance-sorbent, equal to  $\sim 1 : 100$  was used. All solvents (reagent grade,  $>99.5\%$ ) were purchased from commercial sources and used without addition purification.