

**Supporting Information for**  
**Characterizing Nitrilimines with Nuclear Magnetic Resonance Spectroscopy.**

**A Theoretical Study**

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TABLE S1: Normalized Contributions (Weight Percent) of the Three Main Resonance Structures for Nitrilimines,  $R^1-CNN-R^2$ ; Raw Values given in Parentheses.<sup>a</sup>

$R^1$	$R^2$	RS-A	RS-D	RS-C
H	H	40 (36)	44 (39)	16 (14)
BH <sub>2</sub>	H	39 (34)	37 (32)	23 (20)
CH <sub>3</sub>	H	42 (36)	48 (41)	9 (8)
NH <sub>2</sub>	H	31 (27)	35 (31)	34 (30)
OH	H	36 (30)	36 (30)	28 (24)
F	H	35 (30)	29 (24)	36 (30)
H	BH <sub>2</sub>	40 (36)	54 (48)	6 (6)
H	CH <sub>3</sub>	41 (36)	41 (36)	18 (15)
H	NH <sub>2</sub>	41 (33)	27 (22)	32 (25)
H	OH	38 (32)	27 (22)	35 (29)
H	F	37 (32)	27 (24)	35 (31)
BH <sub>2</sub>	BH <sub>2</sub>	39 (35)	43 (38)	19 (17)
CH <sub>3</sub>	CH <sub>3</sub>	44 (36)	46 (37)	10 (8)
NH <sub>2</sub>	NH <sub>2</sub>	14 (12)	13 (11)	73 (61)
OH	OH	25 (22)	19 (17)	57 (51)
F	F	26 (22)	19 (16)	55 (47)

<sup>a</sup> Obtained from Natural Resonance Theory,<sup>1-3</sup> using the PBE0/6-311++G(2df,pd)

electron density and **RS-C** as a reference configuration. See Scheme 1 in the paper for the definition of the resonance structures.

#### References

1. Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 593.
2. Glendening, E. D.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 610.
3. Glendening, E. D.; Badenhoop, J. K.; Weinhold, F. *J. Comput. Chem.* **1998**, *19*, 628.

TABLE S2: Components of the Diagonalized  $^{13}\text{C}$  Shielding Tensor (ppm) and Associated Scalar Descriptors  $\Omega$  (ppm) and  $\kappa$  in Acetylenes and Nitriles.<sup>a</sup>

	$\sigma_{xx}$	$\sigma_{yy}$	$\sigma_{zz}$	$\Omega$	$\kappa$
R			R-C $\equiv$ C-H		
H	279	32	32	247	1.00
BH <sub>2</sub>	293	-10	-12	304	0.99
CH <sub>3</sub>	293	12	12	281	1.00
NH <sub>2</sub>	291	27	0	291	0.81
OH	289	-3	10	292	0.91
F	287	-1	-1	288	1.00
R			R-C $\equiv$ N		
H	279	-23	-23	302	1.00
BH <sub>2</sub>	292	-57	-60	352	0.98
CH <sub>3</sub>	291	-41	-41	332	1.00
NH <sub>2</sub>	287	-28	-39	327	0.93
OH	288	-35	-30	327	0.94
F	286	-27	-27	313	1.00

<sup>a</sup> Calculated for the italicized carbon atom with GIAO-PBE0/6-311++G(2df,pd). In the coordinate system used,  $\sigma_{xx}$  is the parallel component and  $\sigma_{yy}$  and  $\sigma_{zz}$  are the perpendicular components.

TABLE S3: Diamagnetic and Paramagnetic Contributions (ppm) to the  $^{13}\text{C}$  Shielding Tensor Components in Acetylenes, Nitriles and  $\text{BH}_2$ -substitued Nitrilimines.<sup>a</sup>

	$\sigma_{xx}$		$\sigma_{yy}$		$\sigma_{zz}$	
	dia	para	dia	para	dia	para
R	R-C $\equiv$ C-H					
H	279	0	273	-241	273	-241
BH <sub>2</sub>	286	7	285	-295	283	-295
CH <sub>3</sub>	287	7	202	-191	202	-190
NH <sub>2</sub>	288	2	233	-206	231	-232
OH	286	2	240	-243	241	-231
F	287	0	242	-243	242	-243
R	R-C $\equiv$ N					
H	279	0	259	-281	259	-281
BH <sub>2</sub>	285	7	267	-324	265	-325
CH <sub>3</sub>	285	5	252	-293	252	-293
NH <sub>2</sub>	288	0	247	-274	246	-285
OH	287	1	249	-284	249	-279
F	286	0	249	-277	249	-277
BH <sub>2</sub> -CNN-H	287	-68	245	-225	245	-199
H-CNN-BH <sub>2</sub>	282	-87	241	-145	241	-159
BH <sub>2</sub> -CNN-BH <sub>2</sub>	287	-100	239	-189	240	-197

<sup>a</sup> Calculated for the italicized carbon atom with GIAO-PBE0/6-311++G(2df,pd). In the coordinate system used,  $\sigma_{xx}$  is the parallel component,  $\sigma_{yy}$  and  $\sigma_{zz}$  are the perpendicular components.

TABLE S4: Cartesian Coordinates for Nitrilimines.

		H-CNN-H 7 -0.054630 0.000810 -0.016370 7 1.174360 0.043390 0.042010 6 -1.228820 -0.031550 0.130060 1 1.572230 -0.623200 -0.622120 1 -2.037400 0.503110 -0.337710
H <sub>2</sub> B-CNN-H 7 0.569840 -0.147200 0.032330 7 1.794620 -0.279190 0.042110 6 -0.576240 0.122940 -0.023880 1 2.027110 -1.231830 0.335410 5 -1.999750 0.458470 -0.093690 1 -2.314400 1.557340 -0.433010 1 -2.807740 -0.370770 0.188310	H-CNN-BH <sub>2</sub> 7 -0.489810 0.255420 0.199430 7 0.750460 0.130360 0.254940 6 -1.627010 0.443910 0.245550 5 1.432850 -0.752810 -0.605750 1 -2.674670 0.622900 0.279680 1 0.829090 -1.403160 -1.415540 1 2.618850 -0.819550 -0.489250	H <sub>2</sub> B-CNN-BH <sub>2</sub> 7 0.045060 0.058510 0.097790 7 1.219920 -0.231050 0.193320 6 -1.074190 0.415050 0.113690 5 2.179780 -1.012200 -0.432740 5 -2.479720 0.869520 0.117480 1 -2.772800 1.842550 -0.504990 1 -3.287370 0.253170 0.738820 1 1.865430 -1.660530 -1.390920 1 3.284720 -1.004330 0.013480
H <sub>3</sub> C-CNN-H 7 0.647740 -0.191310 0.099810 7 1.887520 -0.192070 0.220730 6 -0.523540 -0.171490 0.175030 1 2.286710 -0.830310 -0.468520 6 -1.764430 0.454140 -0.277170 1 -1.581030 1.317630 -0.924450 1 -2.369400 -0.274520 -0.821330 1 -2.355270 0.774980 0.583350	H-CNN-CH <sub>3</sub> 7 -0.566850 0.266750 0.275790 7 0.585570 -0.050400 0.523010 6 -1.740890 0.440510 0.158510 6 1.330170 -0.566970 -0.619800 1 -2.257750 1.351700 -0.104650 1 0.809950 -1.416880 -1.076410 1 1.478000 0.204630 -1.383070 1 2.303080 -0.895190 -0.259730	H <sub>3</sub> C-CNN-CH <sub>3</sub> 7 0.058550 -0.012630 0.319390 7 1.271130 -0.135190 0.510270 6 -1.123510 0.025860 0.289300 6 1.970400 -0.816770 -0.570420 6 -2.219610 0.903180 -0.139960 1 -1.865180 1.875050 -0.497620 1 -2.785620 0.416550 -0.937380 1 -2.915440 1.059540 0.686750 1 1.574540 -1.829010 -0.725130 1 1.900730 -0.269790 -1.518450 1 3.019510 -0.891270 -0.289340

TABLE S4 Continued

H <sub>2</sub> N - CNN - H	H - CNN - NH <sub>2</sub>	H <sub>2</sub> N - CNN - NH <sub>2</sub>
7 0.615660 -0.125300 0.046930	7 -0.565940 0.241410 0.224980	7 -0.048870 -0.292040 0.065210
7 1.804250 -0.117460 -0.316420	7 0.569270 -0.073110 0.531760	7 1.101970 0.142780 0.184010
6 -0.467830 0.199230 0.452770	6 -1.754520 0.383860 0.047000	6 -1.174420 0.037670 0.648810
1 2.194970 -1.050820 -0.147250	7 1.318350 -0.604220 -0.525310	7 2.046740 -0.660380 -0.382260
7 -1.712520 0.141270 -0.026270	1 -2.149980 1.362680 -0.224090	7 -2.054110 0.700610 -0.072930
1 -1.887810 0.015440 -1.012900	1 1.133600 -0.123950 -1.403040	1 -1.871250 1.054050 -1.008010
1 -2.451870 0.550450 0.513860	1 2.291680 -0.490470 -0.274860	1 -2.967850 0.873100 0.307910
		1 1.703940 -1.268510 -1.120020
		1 2.861590 -0.121420 -0.630910
HO - CNN - H	H - CNN - OH	HO - CNN - OH
7 0.564800 -0.146850 0.098930	7 -0.517270 0.237270 0.285730	7 0.049630 0.073940 0.150540
7 1.758180 -0.090650 0.405160	7 0.690670 0.339740 0.175360	7 1.257260 -0.015560 0.195620
6 -0.633510 -0.307500 0.104640	6 -1.670610 0.078380 0.607400	6 -1.125130 0.203870 0.554490
1 2.307880 -0.539470 -0.336570	8 1.147290 -0.589150 -0.775160	8 1.681040 -1.129190 -0.530860
8 -1.545190 0.494850 -0.438540	1 -2.463900 0.626900 0.101650	8 -1.958400 0.947540 -0.166430
1 -2.406210 0.088190 -0.311560	1 2.095450 -0.422980 -0.772410	1 -2.817090 0.904070 0.262290
		1 2.638520 -1.082810 -0.433970
F - CNN - H	H - CNN - F	F - CNN - F
7 0.533880 -0.134860 0.057700	7 -0.495340 0.254490 0.234300	7 0.053880 0.123090 0.197380
7 1.753630 -0.127690 0.174480	7 0.722980 0.308030 0.279260	7 1.248520 0.107540 0.331000
6 -0.658100 -0.246670 0.293350	6 -1.681960 0.159500 0.408660	6 -1.161020 -0.052490 0.483030
1 2.158420 -0.797180 -0.491420	9 1.211650 -0.627140 -0.655690	9 1.788850 -0.824820 -0.572240
9 -1.580260 0.457230 -0.321540	1 -2.406590 0.749570 -0.145690	9 -2.027820 0.680440 -0.160740