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Supplementary Material

A Comparison of the Lewis Basicity of Diamidocarbenes and Diaminocarbenes

Chin-Hung Lai

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The converged geometry of BH_3

B	0.000000	-0.000030	0.000000
H	0.666771	0.980754	0.000000
H	0.515982	-1.067629	0.000000
H	-1.182753	0.087023	0.000000

The converged geometry of **4**

C	0.000018	-1.271371	0.000000
N	-1.044510	-0.401093	0.000000
C	-0.673414	0.932951	0.000000
C	0.673419	0.932986	0.000000
N	1.044526	-0.401078	0.000000
H	-1.995777	-0.722005	0.000000
H	1.995793	-0.722015	0.000000
H	-1.375769	1.745763	0.000000
H	1.375502	1.746057	-0.000001

The converged geometry of **5**

C	0.000706	-1.327296	0.001645
N	-1.057847	-0.504938	0.073217
C	-0.763481	0.926363	-0.075135
C	0.762556	0.926885	0.075898
N	1.058388	-0.503739	-0.076631
H	-1.994164	-0.861323	0.033534
H	1.994691	-0.859268	-0.028394
H	-1.258971	1.523050	0.688185
H	-1.073378	1.289100	-1.057353
H	1.257258	1.526400	-0.685707
H	1.072090	1.287071	1.059183

The converged geometry of **6**

C	0.000685	-1.783913	0.000000
N	-1.077151	-0.944989	0.000000
C	-0.773525	0.411837	0.000000
C	0.773255	0.412310	0.000000
N	1.078016	-0.944013	0.000000
H	-2.022486	-1.292490	0.000001
H	2.023582	-1.290830	0.000001

O	-1.508464	1.347178	0.000000
O	1.507259	1.348439	0.000000

The converged geometry of **7**

C	-0.000118	1.786560	-0.000001
N	1.127959	1.039861	0.000000
C	1.282294	-0.349929	0.000000
C	0.000197	-1.139662	0.000007
C	-1.282166	-0.349484	-0.000001
N	-1.128834	1.039671	0.000002
H	2.003381	1.544927	-0.000001
H	-2.003882	1.545227	0.000005
H	0.000240	-1.797088	-0.870369
H	0.000239	-1.797068	0.870398
O	2.368412	-0.858137	-0.000005
O	-2.367799	-0.859067	-0.000005

The converged geometry of **8**

C	0.000001	-1.810299	-0.000003
N	1.155291	-1.127274	0.161349
C	1.619411	0.190377	-0.057768
C	0.613625	1.230272	-0.452643
C	-0.613628	1.230260	0.452672
C	-1.619411	0.190375	0.057765
N	-1.155295	-1.127281	-0.161330
H	1.948804	-1.734408	0.323505
H	-1.948804	-1.734414	-0.323507
H	0.321282	1.052155	-1.491178
H	1.130657	2.184539	-0.412091
H	-0.321284	1.052115	1.491201
H	-1.130660	2.184528	0.412143
O	-2.794229	0.411970	-0.055390
O	2.794234	0.411963	0.055348

The converged geometry of **H_3B-4**

B	-2.288915	-0.000023	0.011391
C	-0.695077	0.000028	-0.020135
H	-2.593812	0.002804	1.186443

H	-2.668149	1.010306	-0.537981
H	-2.667933	-1.012958	-0.533303
N	0.134688	-1.056681	-0.012193
C	1.462369	-0.674144	0.010837
C	1.462399	0.674087	0.010836
N	0.134745	1.056705	-0.012198
H	-0.219033	-1.998673	-0.024581
H	2.274058	-1.376558	0.019268
H	2.274124	1.376461	0.019274
H	-0.218860	1.998737	-0.024566

The converged geometry of **H_3B-5**

C	0.764114	-0.005001	-0.031166
N	-0.024525	-1.073847	0.067791
C	-1.442737	-0.759699	-0.078380
C	-1.430084	0.768014	0.111563
N	-0.020463	1.068861	-0.119063
H	0.365664	-1.997388	-0.000052
H	0.380004	1.989571	-0.072767
H	-2.048670	-1.265294	0.669331
H	-1.799236	-1.038769	-1.071637
H	-2.074967	1.281212	-0.597339
H	-1.723798	1.046884	1.125321
B	2.352646	-0.002183	0.018494
H	2.750742	0.967098	-0.585875
H	2.599224	0.099006	1.205037
H	2.754972	-1.056376	-0.417689

The converged geometry of **H_3B-6**

B	2.827808	-0.000003	0.028548
C	1.276674	0.000005	-0.050333
H	2.924353	0.000088	1.251483
H	3.265169	-1.030146	-0.412497
H	3.265188	1.030074	-0.412630
N	0.474315	1.091146	-0.037269
C	-0.881293	0.775148	0.000173
C	-0.881288	-0.775152	0.000173
N	0.474321	-1.091140	-0.037272

H	0.853121	2.026443	-0.051754
O	-1.814068	1.508345	0.022256
O	-1.814060	-1.508352	0.022260
H	0.853136	-2.026434	-0.051766

The converged geometry of **H_3B-7**

C	1.328984	0.000399	-0.029214
N	0.624199	1.143948	-0.021624
C	-0.767028	1.283552	-0.004869
C	-1.535849	-0.000099	0.171677
C	-0.766749	-1.283659	-0.004728
N	0.624169	-1.143179	-0.030698
H	1.164443	1.998878	-0.077083
H	1.164547	-1.997821	-0.089305
H	-1.930092	0.000072	1.191979
H	-2.399410	-0.000402	-0.489799
O	-1.281204	2.359718	-0.096678
O	-1.280728	-2.360341	-0.091546
B	2.900513	-0.000056	0.035166
H	3.058386	-0.006213	1.246407
H	3.319863	-1.022306	-0.446552
H	3.320430	1.026508	-0.436628

The converged geometry of **H_3B-8**

C	0.025471	1.393912	-0.042014
N	-1.158107	0.778982	0.114745
C	-1.638249	-0.535700	-0.068703
C	-0.645228	-1.600885	-0.425782
C	0.579391	-1.595116	0.485962
C	1.610845	-0.594617	0.058729
N	1.179896	0.724777	-0.200853
H	-1.915838	1.439399	0.255143
H	1.960865	1.347876	-0.378791
H	-0.346971	-1.463374	-1.468629
H	-1.177884	-2.544684	-0.355996
H	0.289427	-1.378335	1.517607
H	1.075174	-2.561299	0.477405
O	2.776160	-0.843756	-0.064678

O	-2.814032	-0.730530	0.054521
B	0.075349	2.977480	0.042878
H	0.236194	3.130361	1.242661
H	1.043653	3.371643	-0.560219
H	-0.984294	3.433424	-0.308717

The converged geometry of BH_2

B	0.000000	0.148599	0.000000
H	1.064401	-0.371497	0.000000
H	-1.064401	-0.371498	0.000000

The converged geometry of **H_2B-4**

B	2.278557	0.000235	0.000000
C	0.782347	0.000064	0.000000
H	2.849638	-1.045963	-0.000001
H	2.849124	1.046767	0.000000
N	-0.078254	1.076431	0.000000
C	-1.397130	0.673922	0.000000
C	-1.396818	-0.674059	0.000000
N	-0.077794	-1.076587	0.000000
H	0.251910	2.024003	0.000000
H	0.252516	-2.024124	-0.000001
H	-2.217271	1.366852	0.000000
H	-2.216759	-1.367176	0.000000

The converged geometry of **H_2B-5**

C	0.840384	-0.000048	-0.000097
N	0.017631	-1.087318	0.162581
C	-1.360543	-0.747036	-0.161630
C	-1.360285	0.747164	0.162082
N	0.017664	1.087268	-0.163420
H	0.390166	-1.996451	-0.051955
H	0.390350	1.996238	0.051637
H	-2.070097	-1.308966	0.441227
H	-1.578957	-0.910136	-1.222096
H	-2.070315	1.309185	-0.440122
H	-1.577695	0.910258	1.222755
B	2.343483	-0.000039	0.000286

H	2.917343	-1.037468	0.120065
H	2.917384	1.037399	-0.119198

The converged geometry of **H_2B-6**

B	2.851240	0.000129	0.000000
C	1.345959	0.000448	0.000000
H	3.418223	1.042891	0.000000
H	3.416804	-1.043454	0.000000
N	0.517842	-1.094326	0.000000
C	-0.825989	-0.767862	0.000000
C	-0.826433	0.767663	0.000000
N	0.517277	1.094847	0.000000
H	0.862341	-2.041126	0.000000
H	0.861150	2.041871	0.000000
O	-1.763437	-1.511246	0.000000
O	-1.764285	1.510500	0.000000

The converged geometry of **H_2B-7**

C	1.399169	0.000520	-0.000058
N	0.664070	1.158857	-0.000010
C	-0.709837	1.287942	0.000022
C	-1.493160	-0.000541	-0.000600
C	-0.708903	-1.288455	0.000024
N	0.664905	-1.158356	0.000006
H	1.180276	2.027602	0.000188
H	1.181774	-2.026704	0.000197
H	-2.151420	-0.000793	0.868996
H	-2.149820	-0.000815	-0.871429
O	-1.235755	2.371461	0.000390
O	-1.234060	-2.372340	0.000383
B	2.905048	0.001016	-0.000064
H	3.472697	1.044943	-0.000054
H	3.473332	-1.042588	-0.000065

The converged geometry of **H_2B-8**

C	-0.001167	1.456508	0.000124
N	-1.186872	0.781689	0.187513
C	-1.629442	-0.510195	-0.073853

C	-0.608218	-1.540151	-0.463993
C	0.610070	-1.542075	0.458210
C	1.630215	-0.508454	0.074943
N	1.186987	0.784421	-0.179716
H	-1.962946	1.397791	0.392802
H	1.962251	1.401591	-0.384839
H	-0.302255	-1.365494	-1.498443
H	-1.123002	-2.495934	-0.428377
H	0.303697	-1.374309	1.493658
H	1.126207	-2.496900	0.416768
O	2.806366	-0.752558	-0.039001
O	-2.805011	-0.756415	0.040805
B	-0.003260	2.966582	-0.004294
H	-1.035518	3.536796	0.146378
H	1.027470	3.538765	-0.158080

Table S1. The calculated electronic energies (in hartree), and dipole moments (in debye) for **H_3B-X**, and **H_2B-X** (X = **4**, **5**, **6**, **7**, and **8**).

	The calculated electronic energies (in hartree)[a]	The dipole moment (in debye)
H_3B-4	-252.8526302	6.892
H_3B-5	-254.0511704	7.214
H_3B-6	-402.1108466	0.2811
H_3B-7	-441.4406161	2.831
H_3B-8	-480.7399158	4.553
H_2B-4	-252.2254877	4.509
H_2B-5	-253.4270434	4.384
H_2B-6	-401.5110186	3.940
H_2B-7	-440.8337424	1.120
H_2B-8	-480.1316118	0.5544

a. The value without correcting for the zero-point energy.

Table S2. The calculated vibrational frequencies (in cm^{-1}), and rotational constants (in GHz) for **H_3B-X**, and **H_2B-X** (X = **4**, **5**, **6**, **7**, and **8**).

	The vibrational frequencies (cm^{-1})[A]	The rotational constants (GHz)
H_3B-4	74, 208, 256, 581, 628, 628, 690, 704, 744, 854, 869, 901, 936, 984, 1081, 1134, 1143, 1161, 1165, 1180, 1249, 1300, 1424, 1464, 1546, 1648, 2463, 2494, 2519, 3278, 3298, 3667, 3670	8.695, 3.393, 2.489
H_3B-5	99, 132, 161, 268, 486, 518, 582, 598, 715, 850, 880, 898, 946, 1005, 1034, 1076, 1131, 1137, 1156, 1183, 1222, 1229, 1263, 1315, 1368, 1373, 1506, 1535, 1556, 1588, 2456, 2496, 2528, 3063, 3069, 3124, 3136, 3677, 3687	7.495, 3.151, 2.336
H_3B-6	124, 133, 175, 244, 322, 391, 520, 575, 575, 649, 653, 694, 786, 828, 835, 859, 989, 1064, 1086, 1098, 1156, 1211, 1306, 1337, 1451, 1546, 1937, 1949, 2397, 2533, 2592, 3619, 3623	3.800, 1.866, 1.264

H_3B-7	55, 109, 144, 150, 259, 393, 442, 470, 495, 539, 573, 594, 627, 785, 787, 847, 849, 893, 935, 961, 1041, 1112, 1123, 1166, 1199, 1208, 1232, 1314, 1361, 1404, 1417, 1541, 1573, 1873, 1890, 2428, 2518, 2570, 3071, 3147, 3575, 3580	1.888, 1.880, 0.9573
H_3B-8	67, 114, 137, 152, 188, 262, 330, 339, 448, 479, 531, 568, 579, 631, 739, 790, 802, 827, 843, 875, 906, 969, 994, 1023, 1073, 1118, 1137, 1159, 1178, 1199, 1238, 1266, 1337, 1371, 1395, 1443, 1471, 1481, 1546, 1570, 1869, 1874, 2440, 2515, 2561, 3060, 3073, 3148, 3153, 3534, 3539	1.725, 1.309, 0.7738
H_2B-4	206, 279, 404, 494, 516, 618, 621, 673, 713, 754, 825, 853, 922, 950, 1075, 1137, 1146, 1189, 1270, 1312, 1403, 1426, 1529, 1646, 2616, 2692, 3277, 3298, 3707, 3708	8.776, 3.665, 2.585
H_2B-5	167, 238, 285, 408, 509, 549, 569, 665, 686, 850, 880, 898, 946, 1005, 1034, 1076, 1131, 1137, 1156, 1183, 1222, 1229, 1263, 1315, 1368, 1373,	7.583, 3.388, 2.451

	1506, 1535, 1556, 1588, 2456, 2496, 2528, 3063, 3069, 3124, 3136, 3677, 3687	
H_2B-6	153, 164, 245, 325, 396, 463, 578, 594, 599, 614, 657, 672, 793, 819, 861, 877, 988, 1122, 1183, 1285, 1308, 1340, 1417, 1570, 1875, 1884, 2664, 2751, 3649, 3652	3.848, 1.948, 1.293
H_2B-7	53, 134, 143, 263, 391, 406, 482, 485, 496, 551, 575, 602, 622, 724, 730, 840, 856, 912, 948, 961, 1037, 1190, 1223, 1277, 1304, 1329, 1382, 1392, 1435, 1481, 1604, 1827, 1844, 2652, 2736, 3095, 3134, 3602, 3605	1.987, 1.876, 0.9706
H_2B-8	62, 128, 140, 190, 265, 325, 343, 436, 449, 501, 544, 578, 599, 616, 719, 770, 785, 819, 823, 862, 897, 981, 988, 1050, 1073, 1175, 1177, 1226, 1305, 1307, 1342, 1374, 1408, 1422, 1477, 1478, 1482, 1588, 1821, 1828, 2643, 2727, 3063, 3073, 3146, 3149, 3579, 3582	1.818, 1.302, 0.7859

[A] The value without multiplying a scaling factor.

Computational Methods

In a previous study of the 1,2-H shift in imidazole-2-ylidene,[S1] results at the M06-2X/cc-pVTZ theoretical level showed the least deviation from results obtained at the BD(T)/cc-pVQZ theoretical level. Therefore, M06-2X/cc-pVTZ is suitable for describing the stability and reactivity of carbenes, and thus was used to examine the Lewis basicities of the carbenes in this study. All stationary points were positively identified as equilibrium structures (number of imaginary frequencies = 0).

To investigate bonding differences between the boron-carbenic center in the H_3B-NAC complex and H_3B-NHC complex, natural bond orbital (NBO) and combined charge and bond energy (ETS-NOCV) analyses were performed.[S2] NBOs represent orthonormal sets of localized "maximum occupancy" orbitals, which describe the molecular bonding pattern of electron pairs to yield the most accurate Lewis-like description of the total N-electron density. Except for the BP86 single-point calculations and BP86 ETS-NOCV analyses, all calculations were performed using the Gaussian09 program.[S3] The BP86 single-point calculations and BP86 ETS-NOCV analyses were performed using the Amsterdam Density Functional (ADF) program.[S4] The DZP basis set was chosen for the single-point calculations and ETS-NOCV analyses. Voronoi polyhedra were chosen to perform the numerical integration in the ETS-NOCV analyses (the keyword “te Velde” was set to 5).[S5,S6]

Furthermore, the core shells of all atoms were set to be small. The calculations of the distortion energy are based on the BP86 single-point calculations on the M06-2X-optimized geometries of BH_3 in the **H_3B-X** complexes, carbenes in the **H_3B-X** complexes, free BH_3, and uncomplexed carbenes.

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