Supporting Information

The Boron-Boron Triple Bond?

A thermodynamic and force field based interpretation of the

N-Heterocyclic Carbene (NHC) Stabilization Procedure

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1. Quantum chemical calculations (general remarks)

The geometries of the molecules under discussion were computed within the framework of Density Functional Theory (DFT) at the RI-BP86 level [S1,S2] using a def-SV(P) basis set [S3,S4] for each atom. Vibrational frequency calculations were performed on the optimized structures at this level of theory by diagonalization of the analytically computed Hessian [S5]. For **1** small imaginary frequencies (14i as well as 10i cm^{-1}) were found. The associated modes did not, however, involve movements of the C-B-B-C frame, and so the optimized structure and other computed vibrational details were used in the ensuing discussion. All these calculations entailed the use of the TURBOMOLE package [S6].
Transformation of the cartesian force constant matrices into a system of symmetry coordinates and the extraction of the potential energy distributions were performed with the TURBOMOLE module AOFORCE [S5] as well as the program FCT [S7]. In the description of the symmetry coordinates normalization coefficients were omitted to enhance readability.

2. Thermodynamic discussion

2.1 Vapor pressure diagram of B, B_2, B_2*

Reaction enthalpies and entropies

(taken for the calculation of the vapor pressure diagram)
Standard heat of formation und entropies (298 K, values given in $kJ \cdot mol^{-1}$ or $J \cdot mol^{-1} \cdot K^{-1}$). Energy value for B_2* taken from DFT calculation, value of the entropy identical to that of the ground state molecule.

	$\Delta_f H^\circ$	$_fS^\circ$	Lit.	
B $_s$	0	5.8	[S8]	
$B_{1\ g}$	560.0	153.4	[S8]	
$B_{2\ g}(^3\Sigma_g^-)$	829.7	202.0	[S8]	
$B_2{}^*{}_g$ $(^1\Sigma_g^+)$	1275.0	202.0	calc. ΔE:	445.3 (4.61 eV)

Reaction enthalpies and entropies
(298 K, values given in $kJ \cdot mol^{-1}$ or $J \cdot mol^{-1} \cdot K^{-1}$)

	$\Delta_R H^\circ$	$\Delta_R S^\circ$
$B_s = B_g$	560.0	147.6
$2B_g = B_{2g}$	-290.3	-104.8
$B_{2g} = B_2{}^*{}_g$	445.3	0

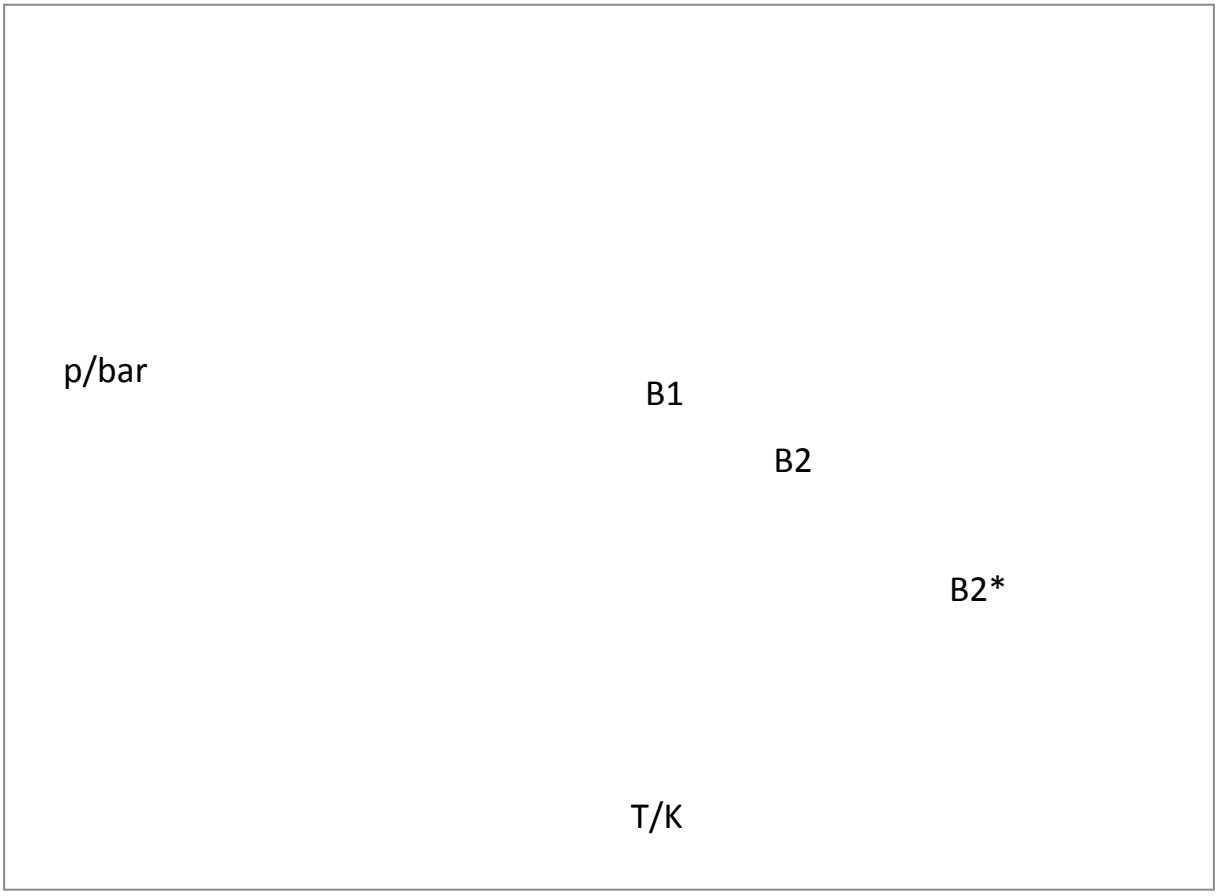

Figure S1: Vapor pressure diagram of B, B_2, $B_2{}^*$

2.2 Further energetic estimations on the grounds of DFT calculations (RI-DFT, BP86, def-SV(P))

B_2 g ($^3\Sigma_g^-$)	-49.366807	a.u.
B_2* g ($^1\Sigma_g^+$)	-49.197197	a.u.
B(^{2}P)	-24.623860	a.u.
B(^{4}P)	-24.504258	a.u.
O_2	-150.226080	a.u.
B_2O_2	-200.093807	a.u.
NHC model	-226.016863	a.u.
NHC complete (of**1**)	-1159.159740	a.u.
NHC complete (of**2**)	-834.847594	a.u.
B-NHC model („monomer“)	-250.687915	a.u.
1a	-501.702948	a.u.
1	-2367.981793	a.u.
2	-1719.417840	a.u.

B_2 ($^3\Sigma_g^-$) + O_2 = B_2O_2	-1315.16 kJ·mol^{-1}
B_2*($^1\Sigma_g^+$) + O_2 = B_2O_2	-1760.48 kJ·mol^{-1}
B(^{2}P) = B(^{4}P)	314.01 kJ·mol^{-1}
B_2 ($^3\Sigma_g^-$) = B_2*($^1\Sigma_g^+$)	445.31 kJ·mol^{-1}
B_2 ($^3\Sigma_g^-$) +2NHC = **1a**	-793.99 kJ·mol^{-1}
B_2 ($^3\Sigma_g^-$) +2 NHC ligand of **1** = **1**	-775.85 kJ·mol^{-1}
2 B-NHC model = **1a**	-858.85 kJ·mol^{-1}
B_2 ($^3\Sigma_g^-$) +2 NHC ligand of **2** = **2**	-934.27 kJ·mol^{-1}

2.3 Energy diagram of 2

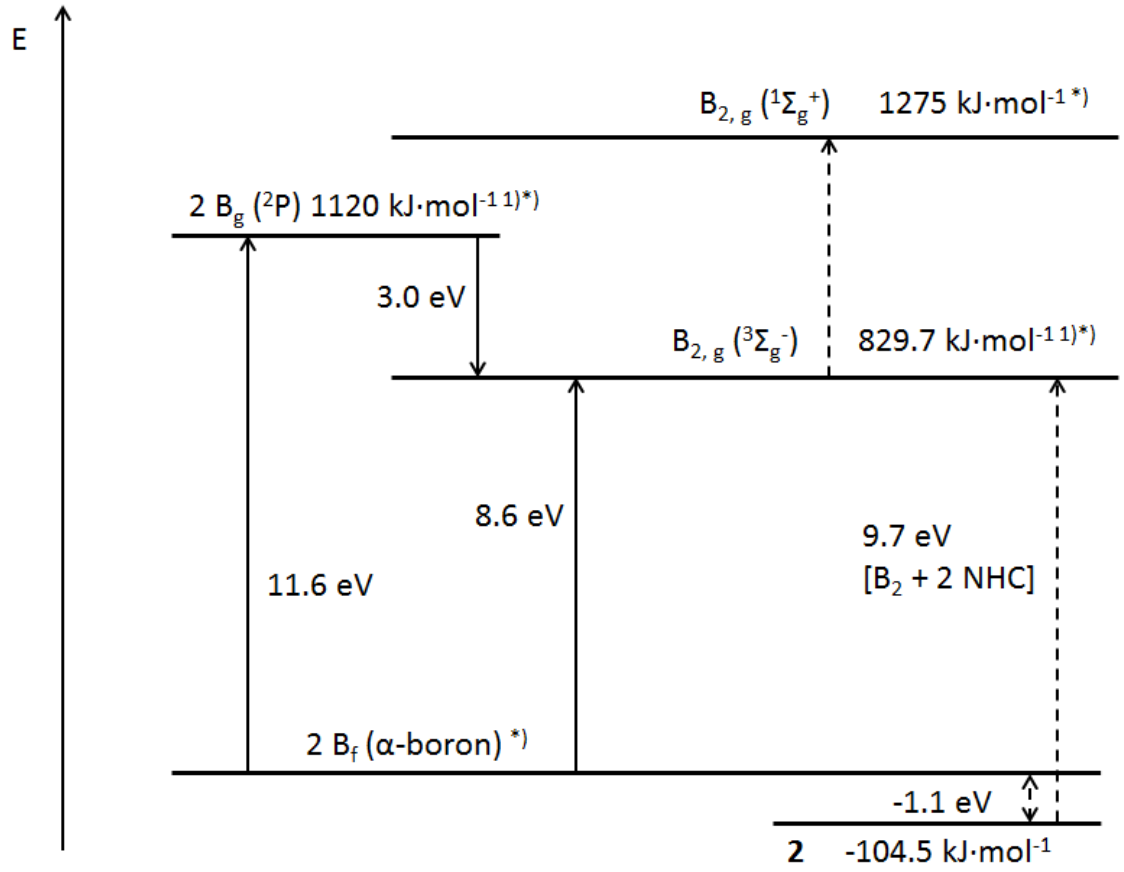

Figure S2: Energy diagram for solid boron, B-atoms, B_2 molecules (B_2, B_2^*) and the decomposition of **2** to B_2 and 2 NHC. Calculated (dashed lines) and experimentally obtained values [S8]. *) "+2 NHC" omitted for clarity; 1) [S8].

3. Quantumchemical calculations for the thermodynamic discussion

3.1 B_2 triplet ground state, $^3\Sigma_g^-$

RI-DFT, BP86, def-SV(P)

D_{6h} symmetry
Occupation:
$alpha 2 a1g 2 a2u 1 e1u
$beta 2 a1g 2 a2u
E_{tot} = -49.3668073856 a. u.
r = 3.0894 a. u. = 163.49 pm

ν = 1020.90 cm^{-1}

f=3.319 mdyn·$Å^{-1}$ using M(B)= 10.811 g·mol^{-1}

3.2 B_2 singlet excited state, $^1\Sigma_g^+$

RI-DFT, BP86, def-SV(P)

D_{6h} symmetry
Occupation:
2 a1g 1 a2u 1 e1u

E_{tot} = -49.1971966959 a. u.

r = 2.6369 a. u. = 139.54 pm

ν = 1552.43 cm^{-1}

f=7.674 mdyn·$Å^{-1}$using M(B)= 10.811 g·mol^{-1}

3.3 B atom

RI-DFT, BP86, def-SV(P)

Doublet ground state, ^{2}P:
E_{tot} = -24.62385972003 a. u.

Quartet excited state, ^{4}P:
E_{tot} = -24.50425844288 a. u.

3.4 Compound 1

RI-DFT, BP86, def-SV(P)

D_{2d} symmetry
E_{tot} = -2367.9817926390 a. u.

r(4 c -- 6 h) = 2.0694 a.u. = 109.51 pm
r(18 c -- 23 h)= 2.0838 a.u. = 110.27 pm
r(19 c -- 24 h) = 2.0844 a.u. = 110.30 pm
r(30 c -- 31 h) = 2.0983 a.u. = 111.04 pm
r(26 c -- 27 h) = 2.0990 a.u. = 111.07 pm
r(109 c -- 115 h) = 2.1024 a.u. = 111.25 pm
r(30 c -- 33 h) = 2.1036 a.u. = 111.32 pm
r(109 c -- 127 h) = 2.1040 a.u. = 111.34 pm
r(109 c -- 121 h) = 2.1046 a.u. = 111.37 pm
r(4 c -- 5 c) = 2.5819 a.u. = 136.63 pm
r(2 n -- 4 c) = 2.6362 a.u. = 139.50 pm
r(18 c -- 19 c) = 2.6507 a.u. = 140.27 pm
r(2 n -- 8 c) = 2.6608 a.u. = 140.80 pm
r(17 c -- 18 c) = 2.6638 a.u. = 140.96 pm
r(17 c -- 22 c) = 2.6832 a.u. = 141.99 pm
r(2 n -- 22 c) = 2.7102 a.u. = 143.42 pm
r(1 b -- 9 b) = 2.8349 a.u. = 150.02 pm
r(1 b -- 8 c) = 2.8383 a.u. = 150.20 pm
r(17 c -- 26 c) = 2.8898 a.u. = 152.92 pm
r(26 c -- 30 c) = 2.9101 a.u. = 153.99 pm
r(26 c -- 35 c) = 2.9210 a.u. = 154.57 pm

3.5 Compound 1a

RI-DFT, BP86, def-SV(P)

D_{2d} symmetry
E_{tot} = -501.7029484714 a. u.

r(2 n -- 6 h) = 1.9273 a.u. = 101.99 pm
r(4 c -- 8 h) = 2.0698 a.u. = 109.53 pm
r(4 c -- 5 c) = 2.5910 a.u. = 137.11 pm
r(3 n -- 5 c) = 2.6270 a.u. = 139.02 pm
r(2 n -- 10 c) = 2.6373 a.u. = 139.56 pm
r(1 b -- 11 b) = 2.8040 a.u. = 148.38 pm
r(1 b -- 10 c) = 2.8172 a.u. = 149.08 pm

3.6 Compound 2

RI-DFT, BP86, def-SV(P)

C_2 symmetry
E_{tot} = -1719.417840 a. u.

Selected internal geometry parameters:

r(106 b -- 53 b) = 2.8714 a.u. = 151.95 pm
r(53 b -- 3 c) = 2.7825 a.u. = 147.25 pm
r(3 c -- 7 n) = 2.6117 a.u. = 138.21 pm
r(3 c -- 4 c) = 2.9179 a.u. = 154.41 pm
r(4 c -- 1 c) = 2.9372 a.u. = 155.43 pm
r(1 c -- 2 c) = 2.9294 a.u. = 155.02 pm
r(7 n -- 2 c) = 2.8501 a.u. = 150.82 pm
r(7 n -- 24 c) = 2.7269 a.u. = 144.30 pm
<(56 c - 53 b - 106 b) = 4.15°
torsion (60 n - 56 c - 3 c - 7 n) = -97.03°
torsion (56 c - 106 b - 53 b - 3 c) = -26.56°

4. Quantumchemical calculations for the force constant discussion

4.1 Vibrational data

4.1.1 Vibrations of 1

irrep.	ν/cm^{-1}	ir intensity/km·mol^{-1}
e	-14.11	0.00000
e	-14.11	0.00000
b1	-9.92	0.00000
	-0.00	0.00000
	0.00	0.00000
	0.00	0.00000
	0.00	0.00000
	0.00	0.00000
	0.00	0.00000
a2	6.52	0.00000
e	13.64	0.16160
e	13.64	0.16160
a1	15.08	0.00000
b1	21.18	0.00000
e	22.56	0.00645
e	22.56	0.00645
e	26.62	0.00092
e	26.62	0.00092
b2	27.94	0.01319
a2	29.84	0.00000
e	36.30	0.02832
e	36.30	0.02832
a1	38.00	0.00000
b2	44.07	0.06756
a2	51.48	0.00000
b1	54.47	0.00000
b1	70.61	0.00000
b2	73.06	1.79772
e	78.60	0.00013
e	78.60	0.00013
a1	79.66	0.00000
e	104.91	5.76821
e	104.91	5.76821
a1	111.75	0.00000
b2	117.89	0.77407
a2	123.56	0.00000
e	131.41	1.02306

e	131.41	1.02306
b1	136.59	0.00000
e	150.45	1.87622
e	150.45	1.87622
e	152.98	0.32089
e	152.98	0.32089
a1	177.26	0.00000
e	196.62	7.53999
e	196.62	7.53999
b2	202.67	1.37131
a2	215.89	0.00000
e	220.06	0.71161
e	220.06	0.71161
a1	225.17	0.00000
b1	225.97	0.00000
e	228.11	0.16596
e	228.11	0.16596
b2	229.70	0.05459
a2	233.67	0.00000
b1	235.51	0.00000
a1	235.91	0.00000
e	239.05	0.33241
e	239.05	0.33241
b2	241.46	1.96663
e	242.15	0.14673
e	242.15	0.14673
a1	242.33	0.00000
b2	243.48	0.10314
e	264.80	0.45930
e	264.80	0.45930
a2	266.25	0.00000
e	267.79	0.00112
e	267.79	0.00112
b1	272.45	0.00000
a1	283.86	0.00000
e	289.72	0.14879
e	289.72	0.14879
b2	293.37	2.92721
a2	297.83	0.00000
b1	299.75	0.00000
e	300.98	0.00908
e	300.98	0.00908
a2	304.86	0.00000
b1	309.93	0.00000
e	322.82	0.10709

e	322.82	0.10709
a1	324.67	0.00000
e	377.19	0.37571
e	377.19	0.37571
a2	404.66	0.00000
b1	408.47	0.00000
e	418.04	0.05462
e	418.04	0.05462
b2	423.23	13.27071
e	430.01	0.36401
e	430.01	0.36401
a1	431.82	0.00000
b2	435.51	15.52355
e	435.98	0.13417
e	435.98	0.13417
a1	443.29	0.00000
e	493.95	1.33801
e	493.95	1.33801
a2	510.20	0.00000
b1	511.35	0.00000
e	521.03	1.36326
e	521.03	1.36326
b2	532.39	6.25566
a1	545.04	0.00000
a2	567.54	0.00000
b1	568.56	0.00000
e	575.66	0.05840
e	575.66	0.05840
e	593.33	0.09088
e	593.33	0.09088
b2	601.76	1.67186
a1	609.35	0.00000
b1	617.01	0.00000
a2	617.32	0.00000
e	625.32	0.01475
e	625.32	0.01475
a2	626.42	0.00000
b1	626.79	0.00000
e	638.80	4.71017
e	638.80	4.71017
e	651.44	33.29474
e	651.44	33.29474
e	672.41	8.38197
e	672.41	8.38197
b2	699.49	4.30171

a1	718.78	0.00000
b2	734.12	3.46944
e	740.81	1.18816
e	740.81	1.18816
a1	753.11	0.00000
e	759.07	21.10464
e	759.07	21.10464
b2	767.08	63.39217
a2	771.37	0.00000
b1	771.91	0.00000
b1	800.86	0.00000
a2	800.90	0.00000
e	801.26	3.55712
e	801.26	3.55712
a1	801.97	0.00000
e	803.80	0.30547
e	803.80	0.30547
b2	804.00	27.85001
a1	880.49	0.00000
e	880.64	0.97285
e	880.64	0.97285
b2	881.14	0.41256
a2	889.59	0.00000
e	889.77	0.26257
e	889.77	0.26257
b1	889.83	0.00000
a2	908.25	0.00000
e	908.68	0.26803
e	908.68	0.26803
b1	908.87	0.00000
e	909.68	2.05562
e	909.68	2.05562
b2	910.20	3.56216
a1	910.33	0.00000
e	915.39	19.54247
e	915.39	19.54247
b1	929.89	0.00000
e	930.51	22.32081
e	930.51	22.32081
a2	930.53	0.00000
a1	940.70	0.00000
e	942.45	0.49192
e	942.45	0.49192
b2	942.53	1.41087
a1	943.44	0.00000

a2	943.66	0.00000
e	944.37	4.59483
e	944.37	4.59483
b1	944.62	0.00000
a1	961.76	0.00000
e	961.81	0.06216
e	961.81	0.06216
b2	961.87	0.35703
b2	972.37	2.65778
e	1033.87	0.65194
e	1033.87	0.65194
a1	1037.68	0.00000
b2	1039.87	16.83199
a2	1049.56	0.00000
b1	1049.97	0.00000
e	1052.42	21.53720
e	1052.42	21.53720
b2	1061.68	13.54854
e	1061.98	6.21631
e	1061.98	6.21631
a1	1063.81	0.00000
a1	1089.96	0.00000
e	1097.88	16.79112
e	1097.88	16.79112
b2	1099.14	1.55566
a1	1102.37	0.00000
e	1103.58	3.18623
e	1103.58	3.18623
b1	1104.49	0.00000
a2	1105.06	0.00000
b2	1105.24	7.44332
e	1105.26	0.17108
e	1105.26	0.17108
a1	1109.34	0.00000
e	1137.34	2.98587
e	1137.34	2.98587
b2	1137.66	27.85435
a1	1139.20	0.00000
a2	1148.67	0.00000
b1	1148.89	0.00000
e	1149.04	0.21728
e	1149.04	0.21728
a2	1163.83	0.00000
b1	1164.43	0.00000
e	1164.59	8.38998

e	1164.59	8.38998
e	1191.48	15.39729
e	1191.48	15.39729
b2	1193.39	1.88744
e	1220.71	0.01376
e	1220.71	0.01376
a1	1223.96	0.00000
b2	1227.51	2.95657
a2	1237.46	0.00000
b1	1237.64	0.00000
e	1237.87	9.00964
e	1237.87	9.00964
e	1258.65	5.40149
e	1258.65	5.40149
a1	1295.09	0.00000
b2	1295.53	37.17236
a2	1295.65	0.00000
e	1295.75	1.39531
e	1295.75	1.39531
b1	1296.03	0.00000
e	1296.34	0.09825
e	1296.34	0.09825
a1	1296.81	0.00000
b2	1300.47	82.15901
a2	1300.54	0.00000
b1	1300.96	0.00000
e	1301.62	0.02236
e	1301.62	0.02236
a1	1314.79	0.00000
e	1321.41	26.05099
e	1321.41	26.05099
b2	1335.04	942.38662
a2	1346.10	0.00000
e	1346.39	3.14892
e	1346.39	3.14892
b1	1346.74	0.00000
b2	1346.85	77.48009
e	1347.02	1.88393
e	1347.02	1.88393
a1	1347.58	0.00000
a1	1361.40	0.00000
b1	1367.74	0.00000
a2	1368.22	0.00000
a2	1368.52	0.00000
e	1368.74	9.69235

e	1368.74	9.69235
b1	1368.96	0.00000
e	1369.04	0.79772
e	1369.04	0.79772
e	1369.69	5.51217
e	1369.69	5.51217
b2	1369.72	5.76153
a1	1370.35	0.00000
e	1384.22	117.30871
e	1384.22	117.30871
b2	1401.76	711.36388
a2	1419.08	0.00000
e	1419.90	1.41637
e	1419.90	1.41637
b2	1420.78	15.93936
a2	1425.17	0.00000
e	1425.73	0.06293
e	1425.73	0.06293
b1	1425.95	0.00000
a1	1427.02	0.00000
e	1427.02	0.00957
e	1427.02	0.00957
b2	1427.99	12.19541
b1	1428.65	0.00000
e	1429.75	0.24181
e	1429.75	0.24181
a1	1430.68	0.00000
e	1437.21	17.21586
e	1437.21	17.21586
a2	1437.34	0.00000
b2	1437.88	2.96124
b1	1439.19	0.00000
a2	1439.63	0.00000
a1	1440.14	0.00000
e	1440.17	27.42487
e	1440.17	27.42487
e	1441.09	1.19502
e	1441.09	1.19502
b2	1443.93	0.69801
e	1451.89	12.09410
e	1451.89	12.09410
a1	1452.27	0.00000
b1	1452.71	0.00000
e	1460.51	96.43358
e	1460.51	96.43358

b2	1461.72	9.55430
a1	1464.59	0.00000
a2	1465.59	0.00000
b1	1467.15	0.00000
e	1467.28	0.88154
e	1467.28	0.88154
a1	1568.26	0.00000
b2	1573.58	8.89306
a2	1595.22	0.00000
b1	1595.27	0.00000
e	1595.63	8.20298
e	1595.63	8.20298
e	1598.37	0.49487
e	1598.37	0.49487
a1	1598.93	0.00000
b2	1599.40	4.93691
a1	1649.61	0.00000
a2	2932.81	0.00000
e	2932.90	0.46196
e	2932.90	0.46196
b1	2932.99	0.00000
b2	2933.04	182.84931
e	2933.12	31.28533
e	2933.12	31.28533
a1	2933.37	0.00000
a2	2937.40	0.00000
e	2937.67	16.58196
e	2937.67	16.58196
b2	2937.97	0.56666
b1	2938.85	0.00000
e	2939.08	95.83871
e	2939.08	95.83871
a1	2939.56	0.00000
e	2980.33	1.52438
e	2980.33	1.52438
b2	2980.89	5.24214
a1	2981.03	0.00000
a2	2985.66	0.00000
b1	2985.71	0.00000
e	2986.19	3.69733
e	2986.19	3.69733
a2	3013.17	0.00000
e	3013.42	3.26110
e	3013.42	3.26110
b2	3013.70	2.41274

b1	3014.20	0.00000
e	3014.39	0.00172
e	3014.39	0.00172
a1	3014.52	0.00000
a2	3020.31	0.00000
b1	3020.70	0.00000
e	3021.04	141.60656
e	3021.04	141.60656
e	3021.20	3.96052
e	3021.20	3.96052
b2	3021.40	10.78705
a1	3021.53	0.00000
e	3022.78	9.93818
e	3022.78	9.93818
a2	3022.86	0.00000
b2	3023.00	44.13554
b1	3023.15	0.00000
e	3023.28	77.97092
e	3023.28	77.97092
a1	3023.29	0.00000
a2	3043.91	0.00000
e	3044.08	0.05494
e	3044.08	0.05494
b2	3044.26	19.92780
b1	3047.76	0.00000
e	3047.98	17.60378
e	3047.98	17.60378
a1	3048.17	0.00000
b2	3083.92	1.61650
e	3083.93	1.46050
e	3083.93	1.46050
a1	3083.96	0.00000
a2	3094.97	0.00000
e	3095.06	28.88435
e	3095.06	28.88435
b1	3095.13	0.00000
e	3107.12	45.42267
e	3107.12	45.42267
b2	3107.16	0.06180
a1	3107.22	0.00000
e	3189.90	3.83496
e	3189.90	3.83496
a1	3210.77	0.00000
b2	3210.77	0.13790

4.1.2 Vibrations of 1a

irrep.	ν/cm^{-1}	ir intensity/km·mol^{-1}
e	45.44	8.74478
e	45.44	8.74478
b1	46.93	0.00000
e	126.85	2.91629
e	126.85	2.91629
a1	264.11	0.00000
e	275.89	0.05183
e	275.89	0.05183
a2	456.26	0.00000
e	458.17	5.64116
e	458.17	5.64116
b1	462.81	0.00000
e	499.22	89.21168
e	499.22	89.21168
a2	586.36	0.00000
b1	592.42	0.00000
e	630.76	73.72583
e	630.76	73.72583
e	655.69	53.45591
e	655.69	53.45591
b2	697.27	3.16186
a2	756.84	0.00000
b1	757.72	0.00000
a1	886.32	0.00000
e	887.91	4.55120
e	887.91	4.55120
b2	936.56	70.54921
e	1035.44	54.60672
e	1035.44	54.60672
a1	1083.59	0.00000
b2	1099.21	31.79661
a1	1113.27	0.00000
b2	1125.96	6.73790
a1	1154.93	0.00000
e	1212.81	0.00001
e	1212.81	0.00001
b2	1289.08	208.68244
e	1339.96	14.04069
e	1339.96	14.04069
e	1380.55	1.05321
e	1380.55	1.05321
a1	1445.56	0.00000

b2	1500.94	1571.51396
a1	1582.16	0.00000
b2	1585.25	266.35857
a1	1716.54	0.00000
e	3189.19	1.60218
e	3189.19	1.60218
b2	3209.34	3.35649
a1	3209.34	0.00000
e	3535.61	121.35383
e	3535.61	121.35383
a1	3536.02	0.00000
b2	3536.08	47.65293

4.2 Normal coordinate analysis of 1a

4.2.1 Symmetry coordinates of the a_1 and b_2 representations

a_1

S_1 = r(B-C) + r(B-C)
S_2 = r(N-C) + r(N-C) + r(N-C) + r(N-C)
S_3 = r(N-C_H) + r(N-C_H) + r(N-C_H) + r(N-C_H)
S_4 = r(N-H) + r(N-H) + r(N-H) + r(N-H)
S_5 = r(C_H-H) + r(C_H-H) + r(C_H-H) + r(C_H-H)
S_6 = <(C-N-H) + <(C-N-H) + <(C-N-H) + <(C-N-H)
S_7 = <(N-C_H-H) + <(N-C_H-H) + <(N-C_H-H) + <(N-C_H-H)
S_8 = r(C_H-C_H) + r(C_H-C_H)
S_9 = <(C-N-C_H) + <(C-N-C_H) + <(C-N-C_H) + <(C-N-C_H)
S_{10} = r(B-B)

b_2

S_{11} = r(B-C) - r(B-C)
S_{12} = r(N-C) + r(N-C) - r(N-C) - r(N-C)
S_{13} = r(N-C_H) + r(N-C_H) - r(N-C_H) - r(N-C_H)
S_{14} = r(N-H) + r(N-H) - r(N-H) - r(N-H)
S_{15} = r(C_H-H) + r(C_H-H) - r(C_H-H) - r(C_H-H)
S_{16} = <(C-N-H) + <(C-N-H) - <(C-N-H) - <(C-N-H)
S_{17} = <(N-C_H-H) + <(N-C_H-H) - <(N-C_H-H) - <(N-C_H-H)
S_{18} = r(C_H-C_H) - r(C_H-C_H)
S_{19} = <(C-N-C_H) + <(C-N-C_H) - <(C-N-C_H) - <(C-N-C_H)

"C" denotes the carbene C-atom, "C_H" denotes an olefin C-atom.

4.2.2 Force constant matrices (mdyn/Å, normalized to unit length):

Representation a_1:

```
 5.21478
 0.66413  6.38612
 0.02350  0.50869  6.34585
-0.03328  0.04223  0.02889  6.92332
 0.00334 -0.04238  0.04175 -0.00094  5.59112
 0.03012  0.18976 -0.37300  0.11058 -0.00505  3.36534
 0.00997  0.23315  0.33421 -0.03038 -0.00824  0.13019  3.05797
-0.10460 -0.14028  0.66439 -0.00863  0.06466  0.15098 -0.59278  8.60128
 0.33031  0.31316  0.40388 -0.29965  0.11243  1.06973  0.13333 -2.12169 11.90226
 0.16260 -0.22712 -0.00060  0.00581  0.00255 -0.05025  0.01411 -0.01430  0.12730  6.01973
```

Representation b_2:

```
 5.17416
 0.68165    6.20539
 0.01243    0.47262    6.35335
-0.03373    0.06669    0.02852    6.92231
 0.00726   -0.05116    0.03758    0.00085    5.59110
-0.01539    0.25484   -0.34153    0.09713   -0.00579  3.38061
 0.01968    0.21026    0.32406   -0.02606   -0.00838  0.12846    3.05744
-0.09969   -0.11740    0.66496   -0.00912    0.06689  0.13536   -0.58726    8.59784
 0.37452    0.18306    0.34344   -0.27633    0.11081  1.06527    0.12820   -2.08501   11.84837
```

4.2.3 Potential energy distribution of the vibrations of the a_1 and b_2 representations

mode at 264.11 cm^{-1}	PED
S_1	0.474777
S_2	0.117535
S_9	0.158509
S_{10}	0.236415

mode at 697.27 cm^{-1}	PED
S_{11}	0.262084
S_{12}	0.128390
S_{19}	0.565839

mode at 886.32 cm^{-1}	PED
S_2	0.141440
S_7	0.100705
S_9	0.686886

mode at 936.56 cm^{-1}	PED
S_{11}	0.073951
S_{12}	0.458449
S_{17}	0.175216
S_{19}	0.264306

mode at 1083.59 cm^{-1}	PED
S_7	0.582249
S_8	0.242796
S_9	0.067059

mode at 1099.21 cm^{-1}	PED
S_{12}	0.085409
S_{17}	0.632390
S_{18}	0.197915

mode at 1113.27 cm^{-1}	PED
S_2	0.219606
S_3	0.149775
S_6	0.457374
S_7	0.125584

mode at 1125.96 cm^{-1}	PED
S_{13}	0.516239
S_{16}	0.331076
S_{18}	0.113321

mode at 1154.93 cm^{-1}	PED
S_2	0.222184
S_3	0.595032
S_8	0.064411
S_{10}	0.074314

mode at 1289.08 cm^{-1}	PED
S_{11}	0.402705
S_{13}	0.302619
S_{16}	0.222923

mode at 1445.56 cm^{-1}	PED
S_2	0.204362
S_3	0.223465
S_6	0.382573
S_8	0.067319
S_9	0.016507
S_{10}	0.104087

mode at 1500.94 cm^{-1}	PED
S_{11}	0.226383
S_{12}	0.231656
S_{13}	0.128674
S_{16}	0.253342
S_{18}	0.083711
S_{19}	0.064627

mode at 1582.16 cm^{-1}	PED
S_6	0.105204
S_7	0.184609
S_8	0.607615
S_9	0.044355

mode at 1585.25 cm^{-1}	PED
S_{12}	0.046667
S_{16}	0.131201
S_{17}	0.177741
S_{18}	0.581370
S_{19}	0.030024

mode at 1716.54 cm^{-1}	PED
S_1	0.434604
S_2	0.041676
S_{10}	0.470759

mode at 3209.34 cm^{-1}	PED
S_{15}	0.986281

mode at 3209.34 cm^{-1}	PED
S_5	0.986313

mode at 3536.02 cm^{-1}	PED
S_4	0.996253

mode at 3536.08 cm^{-1}	PED
S_{14}	0.99610

4.3 Calculated structures and vibrations of molecules mentioned in the text

4.3.1 NHC molecule: $CN_2H_2C_2H_2$

RI-DFT, BP86, def-SV(P)

C_{2v} symmetry
E_{tot} = -226.0168626499 a. u.

r(1 n -- 5 h) = 1.9302 a.u. = 102.14 pm
r(3 c -- 7 h) = 2.0720 a.u. = 109.64 pm
r(3 c -- 4 c) = 2.5925 a.u. = 137.19 pm
r(2 n -- 9 c) = 2.5994 a.u. = 137.55 pm
r(1 n -- 3 c) = 2.6367 a.u. = 139.53 pm
r(5 h -- 9 c) = 3.9666 a.u. = 209.91 pm
r(1 n -- 2 n) = 3.9841 a.u. = 210.83 pm
r(3 c -- 5 h) = 4.0418 a.u. = 213.88 pm
r(1 n -- 4 c) = 4.1570 a.u. = 219.98 pm
r(1 n -- 7 h) = 4.1630 a.u. = 220.30 pm
r(3 c -- 8 h) = 4.2475 a.u. = 224.77 pm
r(3 c -- 9 c) = 4.4080 a.u. = 233.26 pm
r(5 h -- 7 h) = 4.8651 a.u. = 257.45 pm

irrep.	ν/cm^{-1}	ir intensity/$km \cdot mol^{-1}$
b2	582.25	14.86239
a2	607.77	0.00000
b2	670.11	15.80734
a2	674.41	0.00000
b2	727.99	172.79080
a2	772.53	0.00000
a1	889.01	4.22531
b1	896.94	3.67192
b1	1015.87	21.37162
a1	1046.94	13.07233
a1	1111.25	12.13871
a1	1143.59	0.34434
b1	1202.36	0.02875
b1	1341.44	1.86485
b1	1371.15	0.32532
a1	1392.18	21.52452
a1	1575.38	1.38664
b1	3175.58	0.00136
a1	3196.04	1.98293
b1	3515.19	93.73863
a1	3515.71	10.96252

4.3.2 B-NHC ("monomer"): $B(CN_2H_2C_2H_2)$

RI-DFT, BP86, def-SV(P)

C_{2v} symmetry
Occupation of MOs:
$alpha 11 a1 1 a2 6 b1 3 b2,
$beta   10 a1 1 a2 6 b1 3 b2

E_{tot} = -250.6879153505 a. u.

r(2 n -- 6 h) = 1.9207 a.u. = 101.64 pm
r(4 c -- 8 h) = 2.0692 a.u. = 109.50 pm
r(4 c -- 5 c) = 2.5715 a.u. = 136.08 pm
r(2 n -- 4 c) = 2.6506 a.u. = 140.26 pm
r(2 n -- 10 c) = 2.6720 a.u. = 141.40 pm
r(1 b -- 10 c) = 2.7635 a.u. = 146.24 pm

4.3.3 B_2Cl_4

RI-DFT, BP86, def-SV(P)

D_{2d} symmetry
E_{tot} = -1890.2434790280 a. u.
r(1 b -- 2 b) = 3.2103 a.u. = 169.88 pm
r(1 b -- 3 cl) = 3.3325 a.u. = 176.35 pm

irrep.	ν/cm^{-1}	ir intensity/km·mol^{-1}
b1	22.42	0.00000
e	89.06	0.51743
e	89.06	0.51743
a1	167.81	0.00000
b2	281.88	4.28924
a1	390.52	0.00000
e	468.34	5.49777
e	468.34	5.49777
b2	716.58	155.09146
e	900.09	261.40130
e	900.09	261.40130
a1	1134.76	0.00000

4.3.3.1 Symmetry coordinates

a_1

S_1 = r(B-B)
S_2 = r(B-Cl) + r(B-Cl) + r(B-Cl) + r(B-Cl)
S_3 = <(Cl-B-Cl) + <(Cl-B-Cl)
- <(B-B-Cl) - <(B-B-Cl) - <(B-B-Cl)) - <(B-B-Cl)

b_2

S_4 = r(B-Cl) + r(B-Cl) - r(B-Cl) - r(B-Cl)
S_5 = <(Cl-B-Cl) - <(Cl-B-Cl)
- <(B-B-Cl) - <(B-B-Cl) + <(B-B-Cl)) + <(B-B-Cl)

4.3.3.2 Force constant matrices (mdyn/Å, normalized to unit length):

a_1:

```
 2.82562
 0.18951         3.97258
-0.09726         0.26164         2.56376
```

b_2:

```
 3.73914
-0.49456         2.39702
```

4.4 H-B=CH_2

RI-DFT, BP86, def-SV(P)

C_{2v} symmetry
E_{tot} = -64.6206111144 a. u.
r(1 c -- 4 h) = 2.0926 a.u. = 110.73 pm
r(1 c -- 5 h)= 2.0926 a.u. = 110.73 pm
r(2 b -- 3 h) = 2.2723 a.u. = 120.25 pm
r(1 c -- 2 b) = 2.6352 a.u. = 139.45 pm

irrep.	ν/cm^{-1}	ir intensity/km·mol^{-1}
b1	366.43	8.22927
b2	591.34	7.97638
b2	681.93	81.83005
b1	874.00	40.03783
a1	1202.97	11.52747
a1	1478.98	50.76333
a1	2762.80	17.86212
a1	3050.10	16.33415
b1	3114.13	4.09390

4.4.1 Symmetry coordinates

a_1
S_1 = r(B-H)
S_2 = r(B-C)
S_3 = r(C-H) + r(C-H)
S_4 = <(B-C-H) + <(B-C-H)

b_1
S_5 = r(C-H) - r(C-H)
S_6 = <(B-C-H) - <(B-C-H)
S_7 = <(linear bending in plane)(H-B-C)

b_2
S_8 = <(linear bending perpendicular to plane)(H-B-C)
S_9 = out of plane(H-H-C-B)

4.4.2 Force constant matrices (mdyn/Å, normalized to unit length):

a_1

```
 4.05890
-0.05030         7.79306
 0.00629         0.03921         5.24824
 0.04137         0.42170        -0.21892         3.70908
```

b_1

```
 5.21403
 0.48143         1.26055
-0.04035        -0.23822         0.06290
```

b_2

```
 4.24517
 0.70069         1.22273
```

4.5 H_2B-CH_3

RI-DFT, BP86, def-SV(P)

C_s symmetry
E_{tot} = -65.8728087113 a. u.
r(4 c -- 6 h) = 2.1009 a.u. = 111.17 pm
r(4 c -- 7 h) = 2.1009 a.u. = 111.17 pm
r(4 c -- 5 h) = 2.1264 a.u. = 112.52 pm
r(1 b -- 2 h) = 2.3156 a.u. = 122.54 pm

r(1 b -- 3 h) = 2.3156 a.u. = 122.54 pm
r(1 b -- 4 c) = 2.9502 a.u. = 156.12 pm

irrep.	ν/cm^{-1}	ir intensity/km·mol^{-1}
a″	184.54	3.21690
a′	508.07	1.50350
a″	655.75	0.31348
a′	954.62	9.99668
a″	1018.71	20.76704
a′	1039.68	61.99312
a′	1188.79	12.69793
a′	1281.57	80.57505
a″	1364.87	5.49261
a′	1416.96	3.65436
a′	2507.27	107.86320
a′	2584.21	157.08940
a′	2877.11	3.62311
a′	2990.81	10.95539
a″	3043.65	10.40803

4.5.1 Symmetry coordinates

a′

S_1 = r(B-C)
S_2 = r(C-H)
S_3 = r(B-H) + r(B-H)
S_4 = r(C-H) + r(C-H)
S_5 = r(H-C-H) + r(H-C-H)
S_6 = r(B-C-H) + r(B-C-H)
S_7 = r(B-C-H)
S_8 = out of plane (CH_3)
S_9 = out of plane (C-BH_2)

4.5.2 Force constant matrix (mdyn/Å, normalized to unit length):

a′

```
 3.94945
 0.05441  4.62190
 0.09458  0.00463  3.56150
 0.06153  0.01029  0.00512  5.01666
 0.39254  0.03191 -0.18872  0.02654  3.97645
 0.22348  0.14693  0.03543 -0.39998  0.09451  9.94812
-0.25405  0.51191 -0.00551 -0.37670 -0.11275  5.02353  3.76315
-0.23546  0.34992 -0.01874 -0.19121 -0.06512  5.90483  3.40789  5.04400
 0.02633  0.04742 -0.01650 -0.02067  0.11421 -0.18741  0.22157 -0.06576  1.08235
```

4.6 BH_3-CO

RI-DFT, BP86, def-SV(P)

C_{3v} symmetry
E_{tot} = -139.8645980534 a. u.
r(5 c -- 6 o) = 2.1710 a.u. = 114.88 pm
r(1 b -- 2 h) = 2.3353 a.u. = 123.58 pm
r(1 b -- 5 c) = 2.8681 a.u. = 151.77 pm

irrep.	ν/cm^{-1}	ir intensity/km·mol^{-1}
e	284.95	3.18724
e	284.95	3.18724
e	773.83	5.99090
e	773.83	5.99090
a1	787.93	20.11289
a1	1031.39	1.78492
e	1036.99	0.30784
e	1036.99	0.30784
a1	2152.45	467.24185
a1	2393.03	0.03332
e	2473.20	27.26981
e	2473.20	27.26981

4.6.1 Symmetry coordinates

a_1
S_1 = r(C-O)
S_2 = r(B-C)
S_3 = r(B-H) + r(B-H) + r(B-H)
S_4 = r(C-B-H) + r(C-B-H) + r(C-B-H)

4.6.2 Force constant matrix (mdyn/Å, normalized to unit length):

a_1

17.99949			
0.52191	3.69462		
-0.08148	0.03052	3.32717	
0.06616	0.63348	0.03040	2.74526

4.7 B_2O_2

RI-DFT, BP86, def-SV(P)

$D_{\infty h}$ symmetry

E_{tot} = -200.0938069698 a. u.

r(1 b -- 3 o) = 2.2923 a.u. = 121.30 pm

r(2 b -- 4 o) = 2.2923 a.u. = 121.30 pm

r(1 b -- 2 b) = 3.1155 a.u. = 164.87 pm

irrep.	ν/cm^{-1}	ir intensity/km·mol^{-1}
Π_u	206.24	2 x 40.14308
Π_g	496.20	0.00000
Σ_g	606.37	0.00000
Σ_u	1915.80	115.28579
Σ_g	2083.62	0.00000

4.7.1 Symmetry coordinates

Σ_g

S_1 = r(B-B)

S_2 = r(B-O) + r(B-O)

Σ_u

S_3 = r(B-O) - r(B-O)

4.7.2 Force constant matrices (mdyn/Å, normalized to unit length):

Σ_g:

3.45827

0.05082 13.85862

Σ_u:

13.95142

4.8 $B_4O_2^{2-}$

RI-DFT, BP86, def-SV(P)

$D_{\infty h}$ symmetry
E_{tot} = -249.6537795365 a. u.
r(3 b -- 5 o) = 2.3877 a.u. = 126.35 pm
r(1 b -- 3 b) = 3.0508 a.u. = 161.44 pm
r(1 b -- 2 b) = 2.8549 a.u. = 151.07 pm

irrep.	ν/cm^{-1}	ir intensity/km·mol^{-1}
Π_u	81.45	2 x 4.62773
Π_g	233.88	0
Σ_g	406.66	0
Π_g	443.27	0
Π_u	482.03	2 x 27.46142
Σ_u	845.62	1.12242
Σ_g	1465.89	0
Σ_u	1724.43	1724.60615
Σ_g	1776.34	0

4.8.1 Symmetry coordinates

Σ_g
S_1 = r(B-B) (central B-B bond)
S_2 = r(B-B) + r(B-B)
S_3 = r(B-O) + r(B-O)

Σ_u
S_4 = r(B-B) - r(B-B)
S_5 = r(B-O) - r(B-O)

4.8.2 Force constant matrices (mdyn/Å, normalized to unit length):

Σ_g:

```
 5.50966
 0.14178    3.75898
-0.05898    0.36149    10.39925
```

Σ_u:

```
 3.64112
-0.36678   10.11361
```

4.9 C_2N_2

RI-DFT, BP86, def-SV(P)

$D_{\infty h}$ symmetry
E_{tot} = -185.5287076046 a.u.
r(1 c -- 3 n) = 2.2214 au = 117.55 pm
r(1 c -- 2 c) = 2.6146 au = 138.36 pm

irrep.	ν/cm^{-1}	ir intensity/km·mol^{-1}
Π_u	254.15	2 x 15.46006
Π_g	662.94	0
Σ_g	880.05	0
Σ_u	2190.08	0.00892
Σ_g	2360.09	0

4.9.1 Symmetry coordinates

Σ_g
S_1 = r(C-C) (central C-C bond)
S_2 = r(C-N) + r(C-N)

Σ_u
S_3 = r(C-N) - r(C-N)

4.9.2 Force constant matrices (mdyn/Å, normalized to unit length):

Σ_g:

7.28818
0.67112 17.34602

Σ_u:

18.27342

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