Supporting Information

Insights into the Mechanism of BN Generation via

Boron Triazide Precursor: A Theoretical Study

Fengyi Liu, Lingpeng Meng, Zheng Sun, Shijun Zheng

Index:

Table S1. Vibrational Frequencies and Rotational Constants for the Reactant, Intermediates, Transition States (Displacement Vectors Corresponding to Imaginary Frequencies are Shown) and Product of $^1\text{B}(\text{N}_3)_3$ Singlet Unimolecular Reaction at B3LYP/6-311+G(d) Level.

Table S2. Vibrational Frequencies and Rotational Constants for the Reactant, Intermediates, Transition States (Displacement Vectors Corresponding to Imaginary Frequencies are Shown) and Product of $^3\text{B}(\text{N}_3)_3$ Triplet Unimolecular Reaction at B3LYP/6-311+G(d) Level.

Table S3. Vibrational Frequencies and Rotational Constants for $^1\text{NB}(\text{N}_3)_2$ and $^3\text{NB}(\text{N}_3)_2$ at CAS(6,5)/6-31G(d) Level.

Table S4. IRC Curves for Reactions 1-14 on the Singlet Decomposition Surface of $^1\text{B}(\text{N}_3)_3$ at B3LYP/6-311+G(d) Level.

Table S5. IRC Curves for Reactions 15-25 on the Triplet Decomposition Surface of $^3\text{B}(\text{N}_3)_3$ at B3LYP/6-311+G(d) Level.

Table S1. Vibrational Frequencies and Rotational Constants for the Reactant, Intermediates, Transition States (Displacement Vectors Corresponding to Imaginary Frequencies are Shown) and Product of $^1\text{B}(\text{N}_3)_3$ Singlet Unimolecular Reaction at B3LYP/6-311+G(d) Level.

Species	Rotational Constant (GHz)	Vibrational Frequencies (cm^{-1})
$^1\text{B}(\text{N}_3)_3$	1.3, 1.3, 0.6	69, 85, 96, 140, 147, 184, 393, 394, 532, 575, 584, 585, 589, 665, 667, 776, 1134, 1143, 1374, 1424, 1433, 2280, 2284, 2303
$^1\text{NB}(\text{N}_3)_2$	8.4, 1.0, 0.9	60, 99, 147, 200, 319, 425, 451, 546, 554, 606, 646, 752, 844, 1122, 1357, 1699, 2235, 2302
$^1\text{N}_3\text{BN}_4$	18.0, 0.6, 0.6	35, 86, 95, 194, 270, 394, 410, 479, 510, 541, 644, 800, 1029, 1253, 1457, 2056, 2197, 2311
<i>cyc</i> - $^1\text{N}_3\text{BN}_2$	22.5, 2.1, 1.9	125, 141, 393, 433, 572, 576, 744, 1143, 1233, 1374, 1711, 2295
$^1\text{NBN}_4$	84.0, 1.5, 1.5	97, 126, 197, 287, 446, 521, 591, 696, 1001, 1309, 1823, 2198
$^1\text{N}_3\text{BN}_2$	87.1, 1.4, 1.4	106, 132, 277, 310, 397, 534, 603, 674, 1078, 1425, 2087, 2279
$^1\text{NBNN}$	4.5, 0.0, 0.0	170, 171, 510, 510, 788, 1965, 2266
$^1\text{BNNN}$	144.6, 5.9, 5.6	173, 545, 555, 978, 1519, 2322
<i>cyc</i> - $^1\text{NBN}_2$	52.5, 7.0, 6.2	178, 328, 609, 653, 1641, 1994
^1BN	51.2	1762
$^1\text{N}_2$	60.1	2444
$^1\text{TS1}$	1.4, 1.0, 0.6	284 <i>i</i> , 47, 54, 60, 98, 123, 140, 211, 252, 283, 417, 520, 550, 560, 594, 631, 752, 976, 1349, 1356, 1567, 2257, 2290, 2416

¹TS2a 4.3, 1.3, 1.0 666*i*, 60, 94, 147, 193, 369, 453, 522, 547, 573, 603, 703, 820, 914, 1370, 1711, 2143, 2296

¹TS2b 4.7, 1.1, 0.9 235*i*, 52, 71, 148, 221, 332, 453, 548, 552, 585, 625, 704, 804, 1153, 1385, 1813, 2191, 2319

¹TS2c 17.5, 0.6, 0.6 485*i*, 56, 73, 130, 154, 244, 292, 323, 461, 506, 531, 644, 932, 1055, 1290, 1715, 2189, 2289

¹TS2d 15.0, 0.6, 0.6 700*i*, 46, 86, 100, 194, 272, 290, 343, 403, 478, 555, 615, 771, 1199, 1460, 1968, 2163, 2296

¹TS3a 22.5, 1.8, 1.7 538*i*, 101, 113, 304, 325, 433, 459, 827, 970, 1336, 1782, 2287

¹TS3b 32.7, 1.7, 1.6 531 *i*, 129, 160, 217, 314, 542, 595, 603, 1068, 1445, 1914, 2289

¹TS3c 87.9, 1.5, 1.5 298*i*, 96, 127, 269, 352, 510, 560, 594, 1001, 1341, 1828, 2191

¹TS3d 64.0, 1.4, 1.4 290*i*, 87, 133, 213, 286, 423, 589, 597, 1011, 1429, 2230, 2298

¹TS3e 125.7, 1.3, 1.3 698*i*, 91, 104, 235, 312, 464, 493, 503, 934, 1591, 2066, 2102

¹TS4a 67.1, 5.6, 5.2 540*i*, 204, 245, 663, 1825, 2086

¹TS4b 29.7, 11.5, 8.3 440*i*, 474, 576, 761, 1314, 1888

¹TS4c 47.8, 8.3, 7.1 598*i*, 417, 426, 654, 1465, 2103

cis-¹TS4d 42.6, 5.5, 4.8 462*i*, 72, 122, 247, 1406, 2283

trans-¹TS4d 110.2, 4.6, 4.4 440*i*, 56, 128, 236, 1399, 2311

Table S2. Vibrational Frequencies and Rotational Constants for the Reactant, Intermediates, Transition States (Displacement Vectors Corresponding to Imaginary Frequencies are Shown) and Product of ${}^3\text{B}(\text{N}_3)_3$ Triplet Unimolecular Reaction at B3LYP/6-311+G(d) Level.

Species	Rotational Constant (GHz)	Vibrational Frequencies (cm^{-1})
${}^3\text{B}(\text{N}_3)_3$	1.3, 1.2, 0.6	43, 72, 86, 104, 140, 155, 242, 380, 435, 549, 571, 575, 581, 622, 666, 721, 887, 1129, 1184, 1393, 1431, 1689, 2277, 2293
${}^3\text{NB}(\text{N}_3)_2$	4.6, 1.2, 0.9	91, 101, 141, 165, 330, 401, 523, 569, 575, 582, 655, 768, 1089, 1182, 1395, 1411, 2270, 2285
<i>cyc</i> - ${}^3\text{N}_3\text{BN}_2$	21.8, 2.0, 1.8	82, 111, 354, 401, 436, 540, 569, 721, 1182, 1357, 1683, 2324
${}^3\text{N}_3\text{BN}_2$	79.5, 1.4, 1.4	78, 150, 224, 324, 350, 494, 554, 697, 1305, 1549, 1789, 2294
${}^3\text{N}_3\text{NBN}$	11.4, 2.4, 2.1	85, 195, 206, 308, 376, 564, 603, 676, 937, 1084, 1445, 2213
${}^3\text{NBNN}$	744.6, 4.4, 4.4	166, 239, 300, 794, 1671, 1944
${}^3\text{BNNN}$	179.9, 5.7, 5.5	154, 176, 550, 797, 1787, 1861
<i>cyc</i> - ${}^3\text{NBN}_2$	45.8, 7.2, 6.2	320, 369, 760, 903, 1168, 1661
${}^3\text{BN}$	53.5	1896
${}^3\text{TS1}$	1.2, 1.2, 0.6	565 <i>i</i> , 36, 72, 88, 95, 135, 153, 227, 357, 407, 534, 561, 572, 576, 613, 658, 775, 1110, 1163, 1394, 1423, 1868, 2278, 2292

$^3\text{TS2}$ 9.6, 0.9, 0.8 957*i*, 62, 96, 142, 212, 267, 378, 433, 507, 561, 566, 765, 873, 1162, 1323, 1567, 1845, 2299

$^3\text{TS3a}$ 28.5, 1.7, 1.7 436*i*, 27, 126, 138, 334, 416, 479, 671, 778, 1329, 1734, 1880

$^3\text{TS3b}$ 19.6, 1.9, 1.7 300*i*, 65, 107, 307, 370, 515, 570, 773, 1101, 1382, 1770, 2321

$^3\text{TS3c}$ 10.5, 2.4, 2.1 355*i*, 73, 166, 280, 456, 523, 581, 734, 920, 1348, 1380, 2242

³TS3d 37.3, 1.4, 1.3 489*i*, 64, 125, 168, 202, 268, 388, 477, 828, 1698, 1948, 1964

³TS3e 11.6, 2.4, 2.0 765*i*, 105, 192, 308, 373, 442, 558, 685, 780, 929, 1470, 2149

³TS4a 48.4, 6.5, 5.7 561*i*, 331, 344, 829, 1604, 1754

³TS4b 50.7, 7.6, 6.6 641*i*, 330, 478, 940, 1252, 2072

³TS4c 94.9, 4.1, 3.9 279*i*, 79, 172, 317, 1553, 2300

³TS4d 122.5, 5.4, 5.2 447*i*, 100, 328, 490, 1634, 1961

Table S3. Vibrational Frequencies and Rotational Constants for ¹NB(N₃)₂ and ³NB(N₃)₂ at CAS(6,5)/6-31G(d) Level.

Species	Rotational Constant (GHz)	Vibrational Frequencies (cm ⁻¹)
¹ NB(N ₃) ₂	4.1, 1.5, 1.1	64, 113, 154, 223, 281, 424, 479, 589, 637, 661, 686, 791, 911, 1022, 1385, 1795, 2393, 2579
³ NB(N ₃) ₂	4.7, 1.3, 1.0	107, 108, 158, 185, 381, 442, 583, 598, 629, 683, 750, 846, 1161, 1247, 1411, 1433, 2492, 2594

Table S4. IRC Curves for Reactions 1-14 on the Singlet Decomposition Surface of ${}^1\text{B}(\text{N}_3)_3$ at B3LYP/6-311+G(d) Level.

Table S5. IRC Curves for Reactions 15-25 on the Triplet Decomposition Surface of ${}^3\text{B}(\text{N}_3)_3$ at B3LYP/6-311+G(d) Level.

Reaction	IRC Curve
15. ${}^3\text{B}(\text{N}_3)_3 \rightarrow {}^3\text{NB}(\text{N}_3)_2 + {}^1\text{N}_2$	<p>The plot shows the reaction coordinate for the decomposition of ${}^3\text{B}(\text{N}_3)_3$. The y-axis is Relative Energy and the x-axis is Reaction Coordinate s in units of $(\text{amu})^{1/2} \text{ bohr}$. The curve starts at the reactant ${}^3\text{B}(\text{N}_3)_3$ at $s = 0.0$, rises slightly to a local maximum at ${}^3\text{TS1}$ at $s = 0.3$, and then decreases to the product ${}^3\text{NB}(\text{N}_3)_2 + \text{N}_2$ at $s = -37.6$.</p>
16. ${}^3\text{NB}(\text{N}_3)_2 \rightarrow \text{cyc-}{}^3\text{N}_3\text{BN}_2 + {}^1\text{N}_2$	<p>The plot shows the reaction coordinate for the decomposition of ${}^3\text{NB}(\text{N}_3)_2$. The y-axis is Relative Energy and the x-axis is Reaction Coordinate s in units of $(\text{amu})^{1/2} \text{ bohr}$. The curve starts at the reactant ${}^3\text{NB}(\text{N}_3)_2$ at $s = -15$, rises to a peak at the transition state ${}^3\text{TS2}$ at $s = 0$, and then decreases to the product $\text{cyc-}{}^3\text{N}_3\text{BN}_2 + \text{N}_2$ at $s = 10$.</p>