Supporting Information

UV-Photoelectron Spectroscopy of BN Indoles: Experimental and Computational Electronic Structure Analysis

Anna Chrostowska,*,§ Senmiao Xu,†,‡ Audrey Mazière,§ Katherine Boknevitz,† Bo Li,† Eric R. Abbey,‡ Alain Dargelos,§ Alain Graciaa,§ and Shih-Yuan Liu†,‡*

†*Department of Chemistry, Boston College, Chestnut Hill, MA 02467, United States*

‡*Department of Chemistry, University of Oregon, Eugene, Oregon 97403-1253, United States*

§*Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux,*
UMR CNRS 5254, Université de Pau
et des Pays de l'Adour, Avenue de l'Université, 64 000 Pau, France

Index **page**

General

All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere using either standard Schlenk techniques or a glove box.

Et_2O, CH_2Cl_2, and CH_3CN were purified by passing through a neutral alumina column under argon. All other chemicals and solvents were purchased and used as received. “External” BN indole **I**,[1] “fused” BN indole **II**[2] were prepared according to the literature procedures.

^{11}B NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer at ambient temperature. ^{11}B NMR chemical shifts are externally referenced to $BF_3{\bullet}Et_2O$ (δ 0). ^{1}H NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer. ^{13}C NMR spectra were recorded on a Unity/Inova 600 spectrometer. IR spectra were recorded on a Bruker FTIP Alpha (ATR mode) spectrometer. UV-vis spectra were recorded on a Agilent Cary 100 UV-vis spectrophotometer with concentration 1.0 X 10^{-4} M in CH_3CN.

Cyclic Voltammetry was conducted on a SP-200 Potentiostat using glassy carbon working electrode, Pt coil counter electrode, and Ag wire pseudo-reference. Experiments were performed using 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in high purity CH_3CN, and conducted under N_2 atmosphere. E_{ox} values were reported as anodic peak potentials internally calibrated to Fc/Fc^+ standard ($E_{1/2} = 0.40$ V vs. SCE[3] under this conditions). CVs were collected at a sweep rate of 50 mV/s. The analyte concentration was ~ 2 mM.

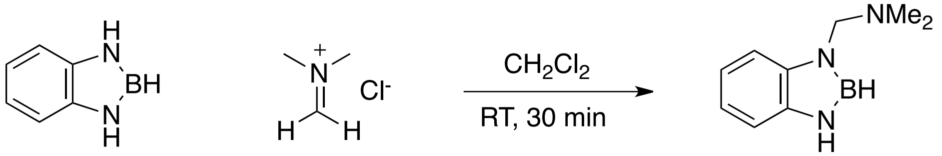
Complete reference 24:

Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

---

(1) Hadebe, S. W.; Robinson, R. S. *Eur. J. Org. Chem.* **2006**, 4898–4904.
(2) Abbey, E. R.; Zakharov, L. N.; Liu, S.-Y. *J. Am. Chem. Soc.* **2011**, *133*, 11508–11511.
(3) Connelly, N. G.; W. E. Geiger. *Chem. Rev.* **1996**, *96*, 877–910.

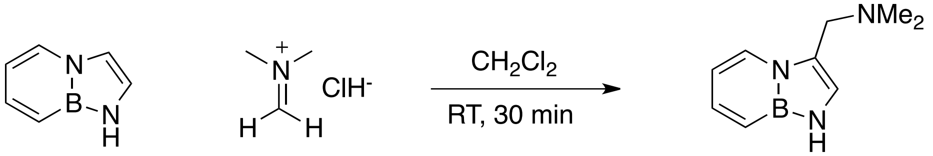
Electrophilic aromatic substitution (EAS) reaction of "external" BN indole I (Figure 5, eq 2)



I

To a 5-mL vial charged with "external" BN indole **I** (23.6 mg, 0.200 mmol) and CH_2Cl_2 (2.0 mL) was added dimethylmethyleneiminium chloride (28.0 mg, 0.300 mmol). The resulting mixture was allowed to stir at room temperature for 0.5 h. The mixture was then passed through an Acrodisc (0.45 μm, PTFE) to remove unreacted iminium salt. Triethylamine (0.1 mL, 0.7 mmol, 3.5 equiv) was then added to release free EAS adduct. After removal of the solvent under reduced pressure, the residue was extracted by ether (3 x 1 mL) to remove ammonium salts. The combined ethereal solution was then concentrated to afford the crude EAS adduct. ^{1}H NMR indicated the reaction was not complete. The molar ratio of **I** to EAS adduct is approximately 1.3:1. We were not able to isolate the EAS adduct by column chromatography due to its instability on either silica gel or alumina. Characteristic ^{1}H NMR and ^{11}B NMR chemical shifts for the EAS adduct: ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 4.36 (s, 2H, NC**H**$_2$N), 2.26 (s, 6H, N(C**H**$_3$)$_2$); ^{11}B NMR (CD_2Cl_2, 160 MHz) δ 25.3 (d, $^2J_{\text{HB}}$ = 166 Hz). HRMS (DART) calcd 176.13590 [(M + H)]$^+$, found 176.13527.

Electrophilic aromatic substitution reaction of "fused" BN indole II (Figure 5, eq 3)



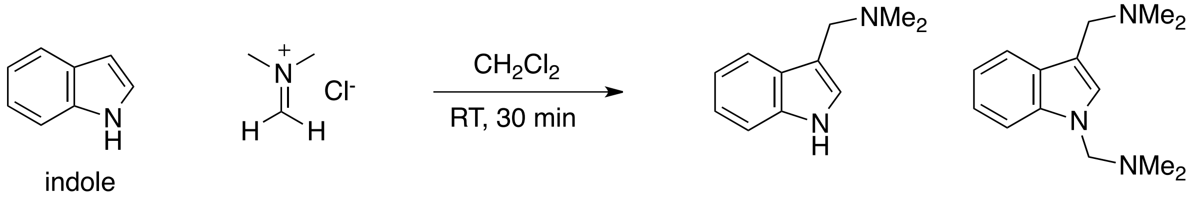
II

To a 5-mL vial charged with "fused" BN indole **II** (23.6 mg, 0.200 mmol) and CH_2Cl_2 (2.0 mL) was added dimethylmethyleneiminium chloride (28.0 mg, 0.300 mmol). The resulting mixture was allowed to stir at room temperature for 0.5 h. After removal of the solvent under reduced pressure, the resulting crude residue was purified by column chromatography on silica gel with Et_2O/Et_3N (80/20) as the eluent to afford the desired EAS adduct as white solid (33.3 mg, 95%).

Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a concentrated solution of BN gramine in Et_2O at –35 °C.

^{1}H NMR (CD_2Cl_2, 500 MHz) δ 8.02 (d, J = 6.5 Hz, 1H), 7.56 (dd, J = 6.0, 1.5 Hz, 1H), 6.69-6.72 (m, 2H), 6.48 (brs, 1H), 6.37 (td, J = 6.5, 1.0 Hz, 1H), 3.51 (s, 2H), 2.21 (s, 6H); ^{13}C NMR (CD_2Cl_2, 150 MHz) δ 138.8, 128.3, 120.9, 119.2, 117.1 (br), 108.5, 55.1, 45.3; ^{11}B NMR (CD_2Cl_2, 162 MHz) δ 23.5; IR (ATR) 3265, 2975, 2943, 2818, 2711, 1623, 1583, 1495, 1466, 1449, 1384, 1339, 1307, 1276, 1248, 1226, 1169, 1144, 1095, 1081, 1035, 996, 845, 813, 708, 692 cm^{-1}.

Electrophilic aromatic substitution reaction of indole (Figure 5, eq 4)



To a 5-mL vial charged with indole (23.4 mg, 0.200 mmol) and CH_2Cl_2 (2.0 mL) was added dimethylmethyleneiminium chloride (28.0 mg, 0.300 mmol). The resulting mixture was allowed to stir at room temperature for 0.5 h. After removal of the solvent under reduced pressure, the resulting crude residue was purified by column chromatography on silica gel with Et_2O/Et_3N (80/20) as the eluent to afford a mixture of gramine and bisalkylated indole (molar ratio: gramine : bisalkylated indole = 2.1: 1) as white solid (34.7 mg, total yield: 90%). The characterization data of gramine[4] and the bisalkylated indole[5] are consistent with those reported in the literature.

Gramine: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.35 (br s, 1H), 7.10 (d, J = 8.5 Hz, 1H), 7.34 (d, J = 8.5 Hz, 1H), 7.19 (td, J = 7.0, 1.0 Hz, 1H), 7.09-7.13 (m, 2H), 3.65 (s, 2H), 2.30 (s, 6H); bisalkylated indole: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.69 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 8.5 Hz, 1H), 7.21 (td, J = 7.0, 1.0 Hz, 1H), 7.09-7.13 (m, 2H), 4.73 (s, 2H), 3.64 (s, 2H), 2.31 (s, 6H), 2.29 (s, 6H).

---

(4) Bandini, M.; Eichholzer, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 9533–9538.
(5) Love, B. E. *J. Org. Chem.* **2006**, *72*, 630–632.

Competitive Electrophilic Aromatic Subistution Experiments (Scheme 2)

General procedueres. To a 5-mL vial charged with 2 different indoles (0.05 mmol for each) and CD_2Cl_2 (1.0 mL) was added dimethylmethyleneiminium chloride (4.7 mg, 0.05 mmol). The resulting mixture was allowed to stir at room temperature for 15 min. The crude ^1H NMR and ^{11}B NMR was then taken to identify relative reactivity between 2 indoles.

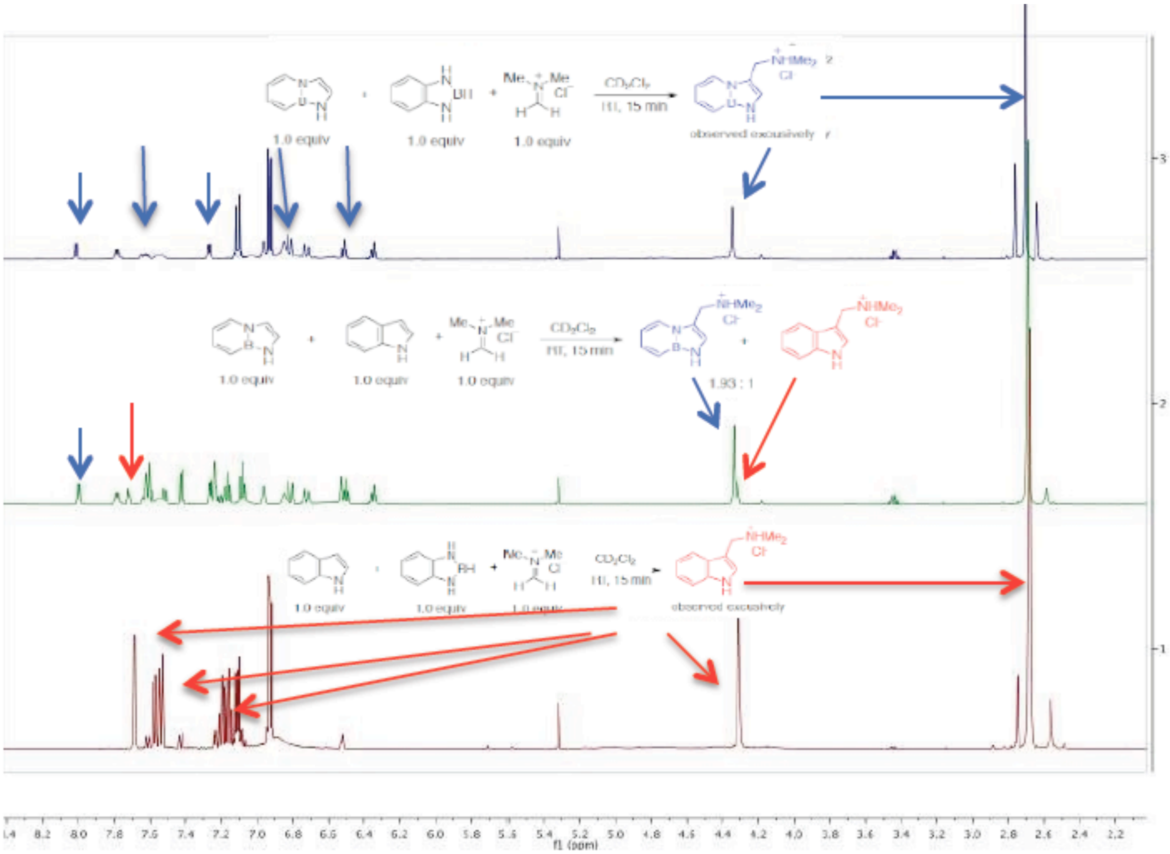


Figure S1. Competitive EAS experiments of "fused" BN indole vs. "external" BN indole (top); "fused" BN indole vs. indole (middle); indole vs. "external" BN indole (bottom). Red arrows point toward signals of the EAS adduct of indole; blue arrows point toward EAS adduct of "fused" BN indole.

Table S1. CAM-B3LYP/6-311G(d,p) geometrical parameters of **Indole**, **I** and **II** (bond angles in Å, angles in degrees).

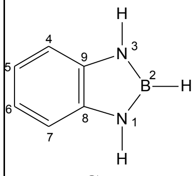
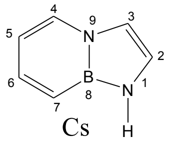
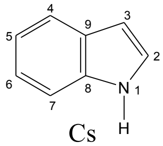
	 C_{2v}		
	I	**II**	**Indole**
Distances:			
1 – 2	1.426	1.386	1.377
2 – 3	1.426	1.349	1.360
3 – 9	1.392	1.396	1.435
9 – 8	1.406	1.454	1.411
8 – 1	1.392	1.435	1.375
9 – 4	1.384	1.361	1.400
4 – 5	1.391	1.358	1.379
5 – 6	1.391	1.428	1.404
6 – 7	1.391	1.365	1.379
7 – 8	1.384	1.504	1.394
Angles:			
4-9-3	131.2	128.7	134.3
3-9-8	108.0	108.9	106.9
8-9-4	120.8	122.4	118.9
9-3-2	109.3	108.3	107.0
3-2-1	105.3	110.4	109.7
2-1-8	109.3	108.7	109.2
1-8-9	108.0	103.7	107.3
1-8-7	131.2	139.1	130.5
7-8-9	120.8	117.2	122.2
8-7-6	118.3	116.4	117.5
7-6-5	121.0	122.9	121.2
6-5-4	121.0	121.3	121.1
5-4-9	118.3	119.8	119.1

Table S2. Atomic coordinates for [CAM-B3LYP/6-311G(d,p)] optimized geometry, value of total energy of Indol

6	1.775070	-1.391599	0.000000
6	0.425124	-1.671498	0.000000
6	-0.489982	-0.612269	0.000000
6	0.000000	0.711320	0.000000
6	1.363939	0.998902	0.000000
6	2.240222	-0.066421	0.000000
6	-1.922114	-0.526228	0.000000
6	-2.240980	0.795439	0.000000
7	-1.089311	1.550160	0.000000
1	2.492652	-2.203129	0.000000
1	0.074780	-2.697215	0.000000
1	1.725270	2.020803	0.000000
1	3.307118	0.121768	0.000000
1	-2.621778	-1.346444	0.000000
1	-3.207834	1.273228	0.000000
1	-1.052706	2.553987	0.000000

E_{TOT} = -363,702677211 au

Table S3. Atomic coordinates for [CAM-B3LYP/6-311G(d,p)] optimized geometry, value of total energy of Molecule I.

6	0.000000	0.695670	-2.125095
6	0.000000	1.411130	-0.932481
6	0.000000	0.702831	0.256963
6	0.000000	-0.702831	0.256963
6	0.000000	-1.411130	-0.932481
6	0.000000	-0.695670	-2.125095
5	0.000000	0.000000	2.445277
7	0.000000	-1.133195	1.580293
7	0.000000	1.133195	1.580293
1	0.000000	1.231628	-3.066235
1	0.000000	2.494971	-0.935192
1	0.000000	-2.494971	-0.935192
1	0.000000	-1.231628	-3.066235
1	0.000000	0.000000	3.628185
1	0.000000	-2.110187	1.815769
1	0.000000	2.110187	1.815769

E_{TOT} = -367,189195686 au

Table S4. Atomic coordinates for [CAM-B3LYP/6-311G(d,p)] optimized geometry, value of total energy of Molecule II.

6	-2.227892	-0.044488	0.000000
6	-1.334349	0.978127	0.000000
7	0.000000	0.709251	0.000000
5	0.520154	-0.648085	0.000000
6	-0.481714	-1.769295	0.000000
6	-1.798025	-1.406407	0.000000
6	1.071945	1.604271	0.000000
6	2.217519	0.892430	0.000000
7	1.943309	-0.465925	0.000000
1	-3.284931	0.185491	0.000000
1	-1.634172	2.019601	0.000000
1	-0.235795	-2.825669	0.000000
1	-2.573124	-2.167711	0.000000
1	0.933041	2.672927	0.000000
1	3.226624	1.272983	0.000000
1	2.679510	-1.148309	0.000000

E_{TOT} = -367,16106098 au

Calculated UV-Vis Spectra (by [CAM-B3LYP/6-311++G(d,p)] with optimized geometry)

Indole

Excited State 1: Singlet-A'	5.0512 eV	245.46 nm	f=0.0401
Excited State 2: Singlet-A'	5.1020 eV	243.01 nm	f=0.1085
Excited State 3: Singlet-A"	5.1763 eV	239.52 nm	f=0.0031
Excited State 4: Singlet-A"	5.6469 eV	219.56 nm	f=0.0050
Excited State 5: Singlet-A"	5.7458 eV	215.78 nm	f=0.0012
Excited State 6: Singlet-A	5.7731 eV	214.76 nm	f=0.0001
Excited State 7: Singlet-A"	6.1133 eV	202.81 nm	f=0.0072
Excited State 8: Singlet-A'	6.2773 eV	197.51 nm	f=0.5347
Excited State 9: Singlet-A"	6.2786 eV	197.47 nm	f=0.0155
Excited State 10: Singlet-A"	6.3673 eV	194.72 nm	f=0.0029
Excited State 11: Singlet-A"	6.4251 eV	192.97 nm	f=0.0038
Excited State 12: Singlet-A'	6.5405 eV	189.56 nm	f=0.3216
Excited State 13: Singlet-A"	6.6633 eV	186.07 nm	f=0.0047
Excited State 14: Singlet-A'	6.7206 eV	184.48 nm	f=0.0688
Excited State 15: Singlet-A"	6.7966 eV	182.42 nm	f=0.0090
Excited State 16: Singlet-A"	6.8352 eV	181.39 nm	f=0.0003
Excited State 17: Singlet-A'	6.9993 eV	177.14 nm	f=0.0512
Excited State 18: Singlet-A"	7.0525 eV	175.80 nm	f=0.0003
Excited State 19: Singlet-A'	7.1101 eV	174.38 nm	f=0.1932
Excited State 20: Singlet-A"	7.1304 eV	173.88 nm	f=0.0016

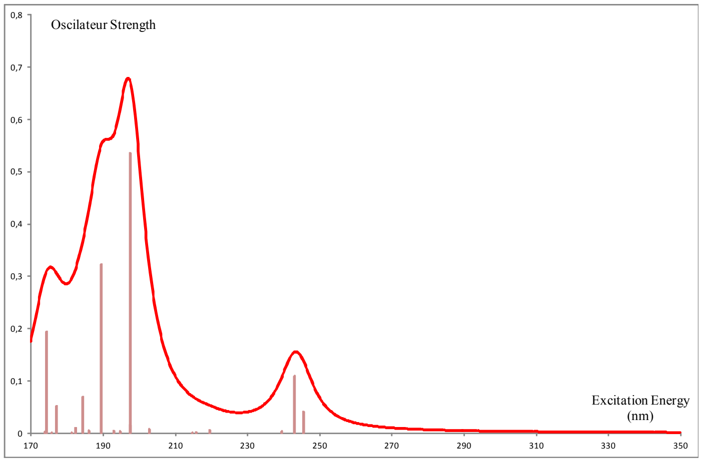


Figure S2: UV-Vis spectrum of **Indole**

External BN Indole I

Excited State 1: Singlet-A1	5.0154 eV	247.21 nm	f=0.1108
Excited State 2: Singlet-B1	5.3816 eV	230.39 nm	f=0.0081
Excited State 3: Singlet-B2	5.5780 eV	222.27 nm	f=0.0043
Excited State 4: Singlet-A2	5.6394 eV	219.85 nm	f=0.0000
Excited State 5: Singlet-B1	5.8765 eV	210.98 nm	f=0.0019
Excited State 6: Singlet-A2	5.9610 eV	207.99 nm	f=0.0000
Excited State 7: Singlet-B1	6.2121 eV	199.58 nm	f=0.0042
Excited State 8: Singlet-A1	6.3460 eV	195.37 nm	f=0.2592
Excited State 9: Singlet-A2	6.3657 eV	194.77 nm	f=0.0000
Excited State 10: Singlet-B2	6.4353 eV	192.66 nm	f=0.3276
Excited State 11: Singlet-B1	6.4664 eV	191.74 nm	f=0.0018
Excited State 12: Singlet-A2	6.4696 eV	191.64 nm	f=0.0000
Excited State 13: Singlet-B1	6.6657 eV	186.00 nm	f=0.0186
Excited State 14: Singlet-A1	6.7733 eV	183.05 nm	f=0.5284
Excited State 15: Singlet-B1	6.8635 eV	180.64 nm	f=0.0129
Excited State 16: Singlet-A2	7.0084 eV	176.91 nm	f=0.0000
Excited State 17: Singlet-A1	7.0955 eV	174.74 nm	f=0.1011
Excited State 18: Singlet-A2	7.1396 eV	173.66 nm	f=0.0000
Excited State 19: Singlet-B2	7.1555 eV	173.27 nm	f=0.0151
Excited State 20: Singlet-B1	7.2384 eV	171.29 nm	f=0.0012

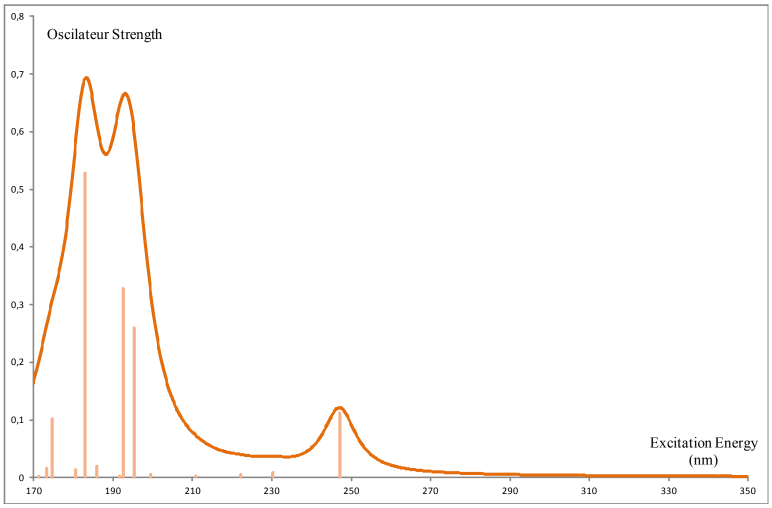


Figure S3: UV-Vis spectrum of **I**.

Fused BN Indole II

Excited State 1: Singlet-A’	4.8408 eV	256.12 nm	f=0.1600
Excited State 2: Singlet-A’	5.0935 eV	243.41 nm	f=0.0819
Excited State 3: Singlet-A″	5.1629 eV	240.14 nm	f=0.0041
Excited State 4: Singlet-A″	5.5313 eV	224.15 nm	f=0.0025
Excited State 5: Singlet-A″	5.6809 eV	218.25 nm	f=0.0140
Excited State 6: Singlet-A″	5.8460 eV	212.08 nm	f=0.0009
Excited State 7: Singlet-A″	5.9269 eV	209.19 nm	f=0.0043
Excited State 8: Singlet-A″	6.1001 eV	203.25 nm	f=0.0055
Excited State 9: Singlet-A’	6.2266 eV	199.12 nm	f=0.2130
Excited State10: Singlet-A’	6.3480 eV	195.31 nm	f=0.2434
Excited State 11: Singlet-A″	6.3608eV	194.92 nm	f=0.0158
Excited State 12: Singlet-A″	6.3872 eV	194.11 nm	f=0.0008
Excited State 13: Singlet-A″	6.5303 eV	189.86 nm	f=0.0010
Excited State 14: Singlet-A″	6.5853 eV	188.27 nm	f=0.0068
Excited State 15: Singlet-A″	6.6145 eV	187.44 nm	f=0.0013
Excited State 16: Singlet-A’	6.6182 eV	187.34 nm	f=0.0563
Excited State 17: Singlet-A″	6.6529 eV	186.36 nm	f=0.0021
Excited State 18: Singlet-A’	6.8437 eV	181.16 nm	f=0.0210
Excited State 19: Singlet-A’	6.9039 eV	179.59 nm	f=0.2411
Excited State 20: Singlet-A’	7.0657 eV	175.47 nm	f=0.0094

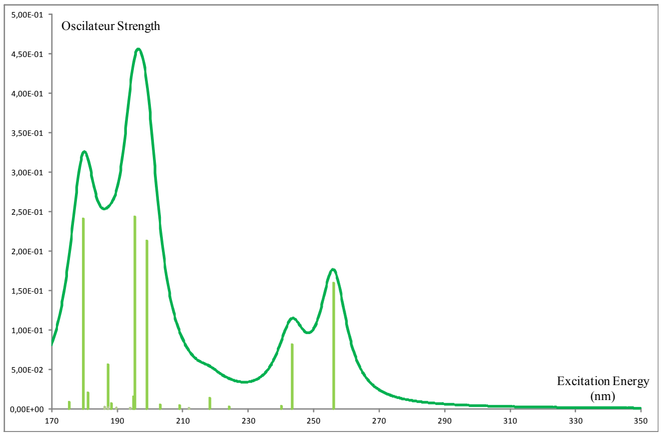


Figure S4: UV-Vis spectrum of **II**.

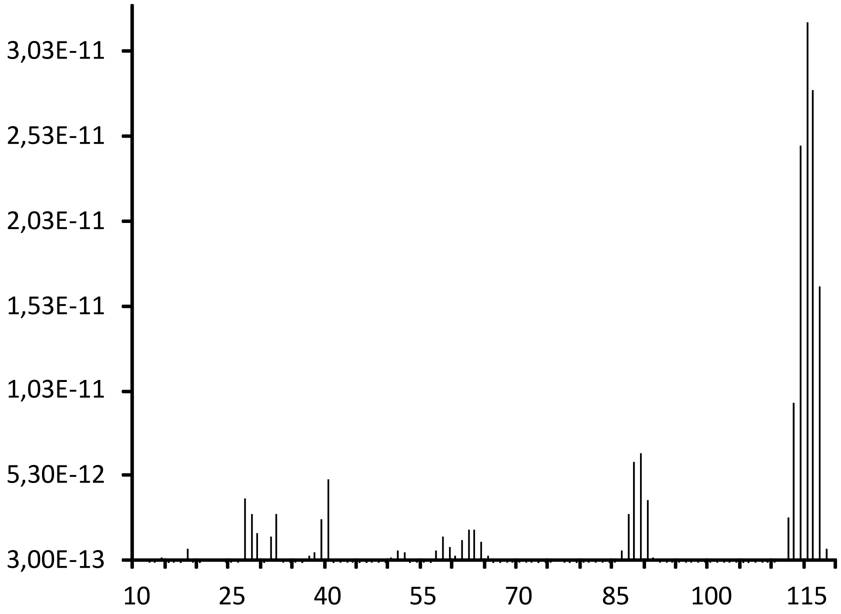


Figure S5: Mass spectrum of **I**.

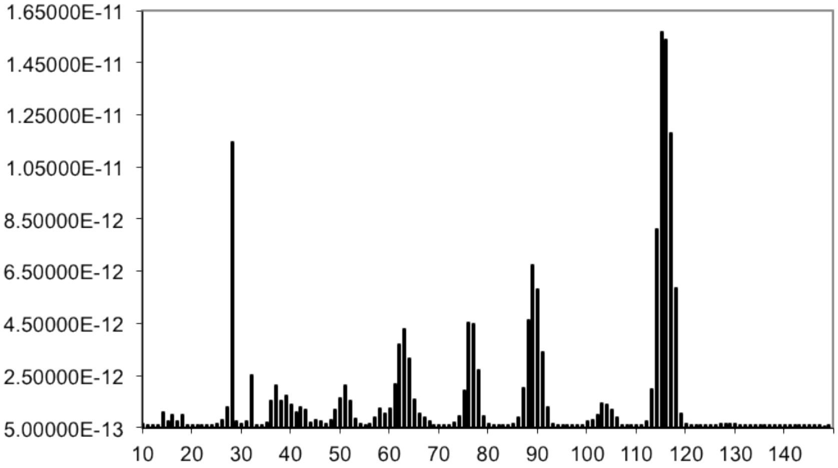
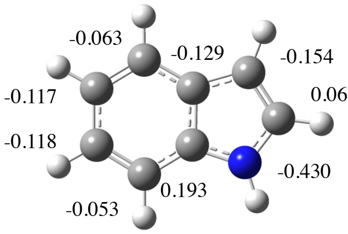
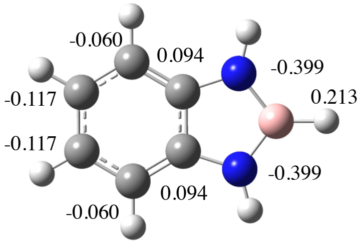


Figure S6: Mass spectrum of **II**.

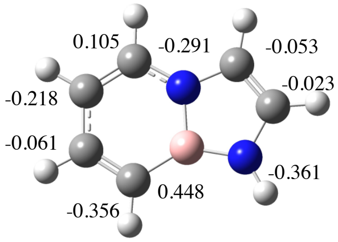
Calculated Mulliken Charges [CAM-B3LYP/6-311G(d,p)]



indole

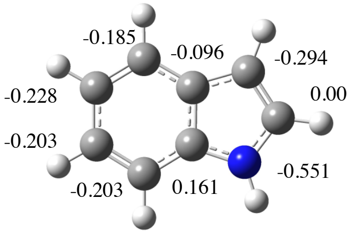


BN indole **I**

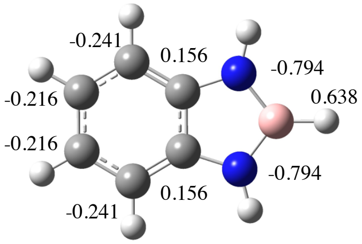


BN indole **II**

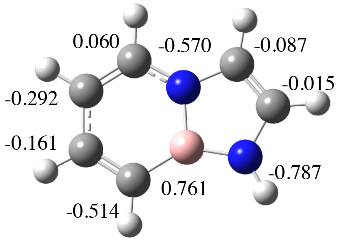
Calculated Natural Charges [CAM-B3LYP/6-311G(d,p)]



indole



BN indole **I**



BN indole **II**

Crystal structure of “fused” BN gramine.

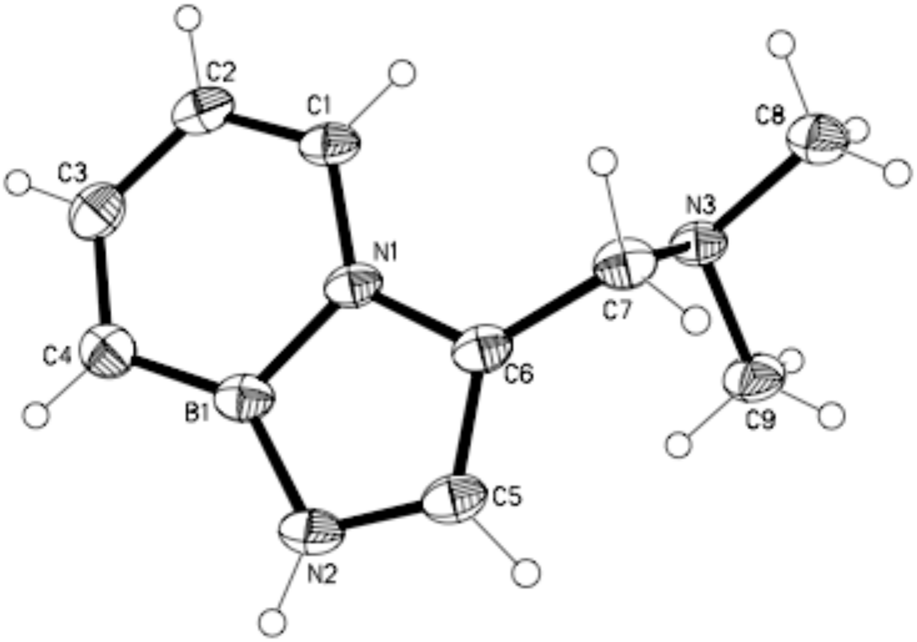


Table S5. Crystal data and structure refinement for BN gramine.

Identification code	C9H14BN3	
Empirical formula	C9 H14 B N3	
Formula weight	175.04	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.0589(17) Å	α= 90°.
	b = 8.5755(14) Å	β= 102.345(4)°.
	c = 11.8802(18) Å	γ = 90°.
Volume	1001.1(3) Å^3	
Z	4	
Density (calculated)	1.161 Mg/m^3	
Absorption coefficient	0.071 mm^{-1}	
F(000)	376	
Crystal size	0.320 x 0.170 x 0.050 mm^3	
Theta range for data collection	2.073 to 30.486°.	
Index ranges	-14<=h<=13, -12<=k<=11, 0<=l<=16	
Reflections collected	5326	
Independent reflections	2838 [R(int) = 0.0604]	
Completeness to theta = 28.000∞	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.4876	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2838 / 1 / 123	
Goodness-of-fit on F^2	1.080	
Final R indices [I>2sigma(I)]	R1 = 0.0551, wR2 = 0.1510	
R indices (all data)	R1 = 0.0666, wR2 = 0.1576	
Extinction coefficient	na	
Largest diff. peak and hole	0.482 and -0.176 e. Å^{-3}	

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for BN gramine. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	4400(1)	-3340(1)	3807(1)	21(1)
N(2)	3894(1)	-5225(1)	2420(1)	26(1)
N(3)	7686(1)	-2707(1)	4254(1)	22(1)
C(1)	4237(1)	-2108(1)	4505(1)	24(1)
C(2)	2997(1)	-1383(2)	4335(1)	28(1)
C(3)	1874(1)	-1862(2)	3452(1)	29(1)
C(4)	1945(1)	-3094(1)	2725(1)	27(1)
C(5)	5234(1)	-5381(1)	3020(1)	25(1)
C(6)	5570(1)	-4273(1)	3852(1)	22(1)
C(7)	6902(1)	-3983(1)	4656(1)	24(1)
C(8)	8846(1)	-2277(2)	5176(1)	29(1)
C(9)	8189(1)	-3218(2)	3237(1)	30(1)
B(1)	3295(1)	-3927(2)	2895(1)	23(1)

Table S7. Bond lengths [Å] and angles [°] for BN gramine.

N(1)-C(1)	1.3740(13)
N(1)-C(6)	1.4147(14)
N(1)-B(1)	1.4654(16)
N(2)-C(5)	1.3898(16)
N(2)-B(1)	1.4378(16)
N(2)-H(2N)	0.881(12)
N(3)-C(8)	1.4663(15)
N(3)-C(9)	1.4737(13)
N(3)-C(7)	1.4859(14)
C(1)-C(2)	1.3690(17)
C(1)-H(1)	0.9500
C(2)-C(3)	1.4278(18)
C(2)-H(2)	0.9500
C(3)-C(4)	1.3767(16)
C(3)-H(3)	0.9500
C(4)-B(1)	1.5092(18)
C(4)-H(4)	0.9500
C(5)-C(6)	1.3607(16)
C(5)-H(5)	0.9500
C(6)-C(7)	1.4906(16)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800

C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(1)-N(1)-C(6)	128.16(10)
C(1)-N(1)-B(1)	122.74(10)
C(6)-N(1)-B(1)	109.07(9)
C(5)-N(2)-B(1)	108.34(10)
C(5)-N(2)-H(2N)	124.7(9)
B(1)-N(2)-H(2N)	126.9(9)
C(8)-N(3)-C(9)	109.25(9)
C(8)-N(3)-C(7)	109.74(8)
C(9)-N(3)-C(7)	110.09(9)
C(2)-C(1)-N(1)	118.84(11)
C(2)-C(1)-H(1)	120.6
N(1)-C(1)-H(1)	120.6
C(1)-C(2)-C(3)	122.07(11)
C(1)-C(2)-H(2)	119.0
C(3)-C(2)-H(2)	119.0
C(4)-C(3)-C(2)	122.83(11)
C(4)-C(3)-H(3)	118.6
C(2)-C(3)-H(3)	118.6
C(3)-C(4)-B(1)	116.45(11)
C(3)-C(4)-H(4)	121.8
B(1)-C(4)-H(4)	121.8
C(6)-C(5)-N(2)	111.63(10)
C(6)-C(5)-H(5)	124.2

N(2)-C(5)-H(5)	124.2
C(5)-C(6)-N(1)	106.99(10)
C(5)-C(6)-C(7)	129.17(11)
N(1)-C(6)-C(7)	123.79(10)
N(3)-C(7)-C(6)	112.54(9)
N(3)-C(7)-H(7A)	109.1
C(6)-C(7)-H(7A)	109.1
N(3)-C(7)-H(7B)	109.1
C(6)-C(7)-H(7B)	109.1
H(7A)-C(7)-H(7B)	107.8
N(3)-C(8)-H(8A)	109.5
N(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
N(3)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
N(3)-C(9)-H(9A)	109.5
N(3)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(3)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
N(2)-B(1)-N(1)	103.97(10)
N(2)-B(1)-C(4)	138.97(11)
N(1)-B(1)-C(4)	117.06(10)

Symmetry transformations used to generate equivalent atoms:

Table S8. Anisotropic displacement parameters ($Å^2$x 10^3) for BN gramine. The anisotropic displacement factor exponent takes the form: $-2p^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	30(1)	19(1)	16(1)	1(1)	9(1)	0(1)
N(2)	36(1)	24(1)	18(1)	-3(1)	7(1)	-3(1)
N(3)	30(1)	23(1)	16(1)	0(1)	9(1)	-1(1)
C(1)	35(1)	22(1)	17(1)	-1(1)	10(1)	-3(1)
C(2)	38(1)	24(1)	25(1)	-2(1)	14(1)	2(1)
C(3)	32(1)	29(1)	29(1)	5(1)	12(1)	3(1)
C(4)	30(1)	29(1)	22(1)	3(1)	6(1)	-3(1)
C(5)	35(1)	22(1)	20(1)	0(1)	11(1)	1(1)
C(6)	30(1)	20(1)	18(1)	2(1)	10(1)	0(1)
C(7)	33(1)	22(1)	18(1)	3(1)	9(1)	1(1)
C(8)	34(1)	31(1)	22(1)	-3(1)	7(1)	-2(1)
C(9)	36(1)	35(1)	21(1)	-4(1)	14(1)	-2(1)
B(1)	33(1)	22(1)	16(1)	2(1)	8(1)	-2(1)

Table S9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for BN gramine.

	x	y	z	U(eq)
H(2N)	3497(13)	-5829(16)	1845(11)	31
H(1)	4971	-1766	5095	28
H(2)	2881	-536	4820	33
H(3)	1041	-1305	3363	35
H(4)	1185	-3403	2146	32
H(5)	5840	-6164	2867	30
H(7A)	6739	-3711	5425	28
H(7B)	7449	-4952	4737	28
H(8A)	9448	-3179	5375	43
H(8B)	8515	-1943	5856	43
H(8C)	9349	-1420	4914	43
H(9A)	8668	-2353	2956	45
H(9B)	7419	-3543	2629	45
H(9C)	8816	-4097	3448	45

Table S10. Torsion angles [°] for BN gramine.

C(6)-N(1)-C(1)-C(2)	-178.16(10)
B(1)-N(1)-C(1)-C(2)	-0.84(15)
N(1)-C(1)-C(2)-C(3)	-0.37(17)
C(1)-C(2)-C(3)-C(4)	1.14(18)
C(2)-C(3)-C(4)-B(1)	-0.62(16)
B(1)-N(2)-C(5)-C(6)	-0.47(12)
N(2)-C(5)-C(6)-N(1)	0.19(12)
N(2)-C(5)-C(6)-C(7)	-177.54(9)
C(1)-N(1)-C(6)-C(5)	177.77(9)
B(1)-N(1)-C(6)-C(5)	0.16(11)
C(1)-N(1)-C(6)-C(7)	-4.35(16)
B(1)-N(1)-C(6)-C(7)	178.04(9)
C(8)-N(3)-C(7)-C(6)	169.08(9)
C(9)-N(3)-C(7)-C(6)	-70.63(12)
C(5)-C(6)-C(7)-N(3)	98.45(13)
N(1)-C(6)-C(7)-N(3)	-78.94(11)
C(5)-N(2)-B(1)-N(1)	0.53(11)
C(5)-N(2)-B(1)-C(4)	-178.75(13)
C(1)-N(1)-B(1)-N(2)	-178.19(8)
C(6)-N(1)-B(1)-N(2)	-0.42(11)
C(1)-N(1)-B(1)-C(4)	1.28(15)
C(6)-N(1)-B(1)-C(4)	179.05(9)
C(3)-C(4)-B(1)-N(2)	178.70(12)
C(3)-C(4)-B(1)-N(1)	-0.52(15)

Symmetry transformations used to generate equivalent atoms:

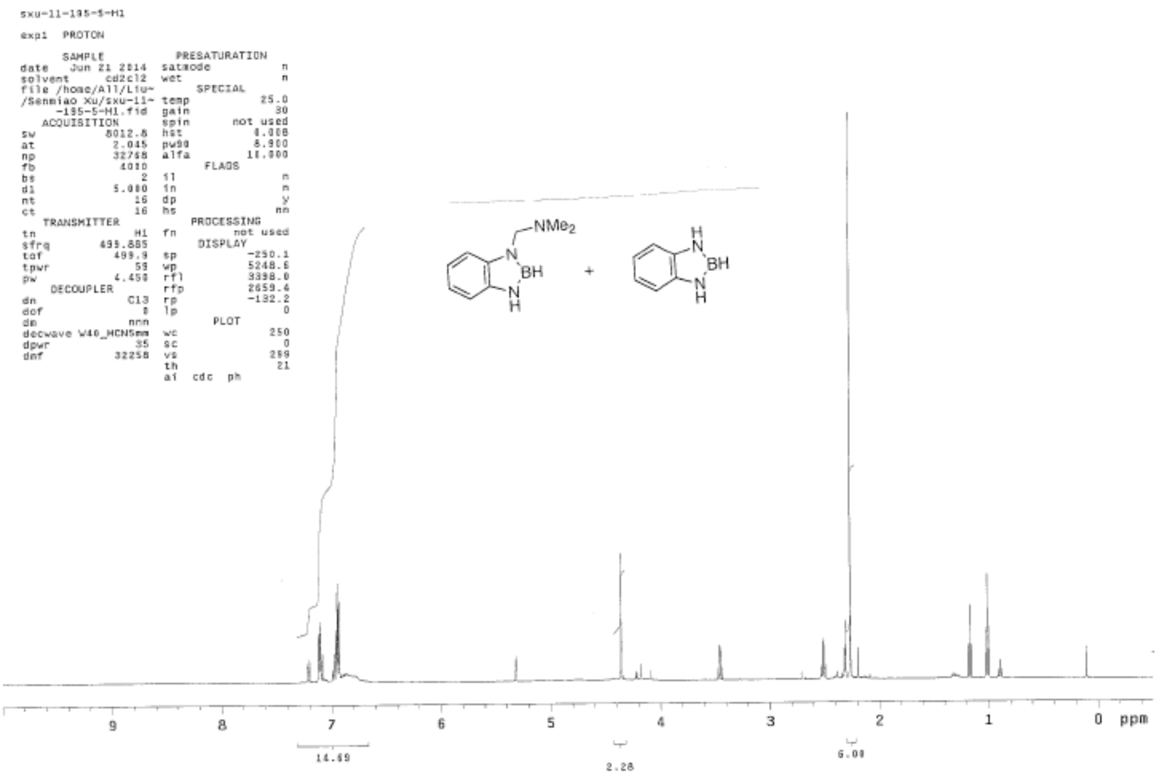
Table S11. Hydrogen bonds for BN gramine [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2N)...N(3)#1	0.881(12)	2.248(13)	3.1079(14)	165.2(12)

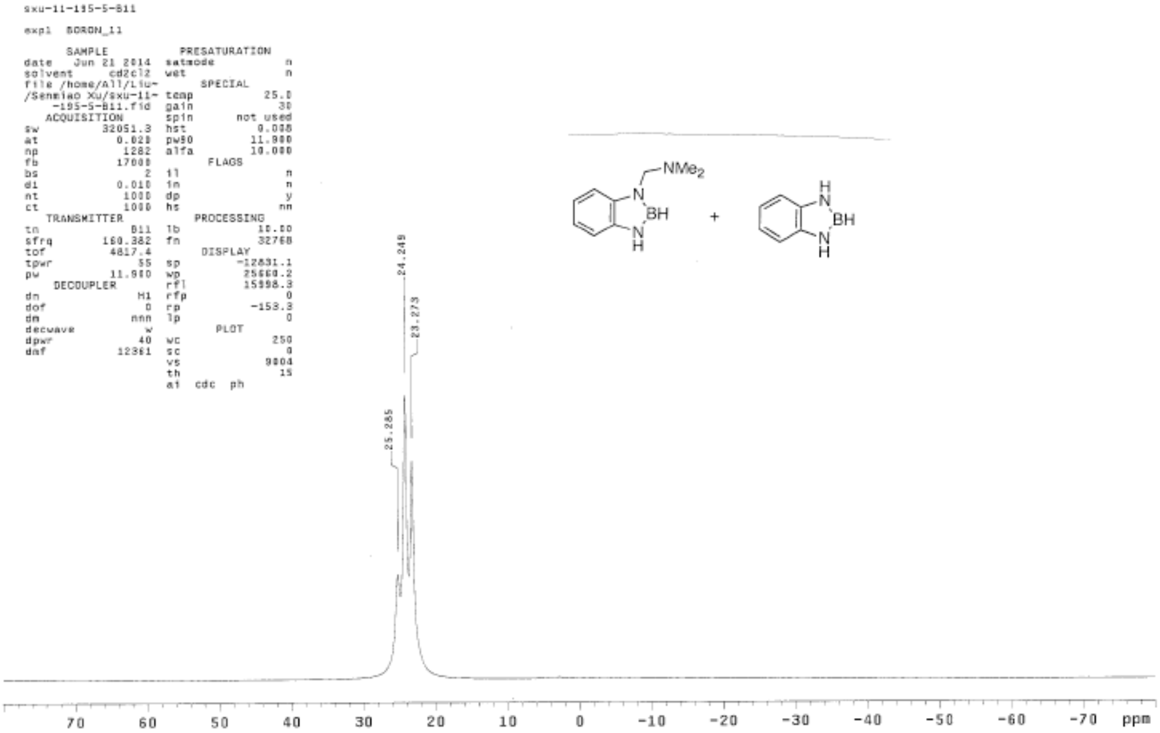
Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y-1/2,-z+1/2

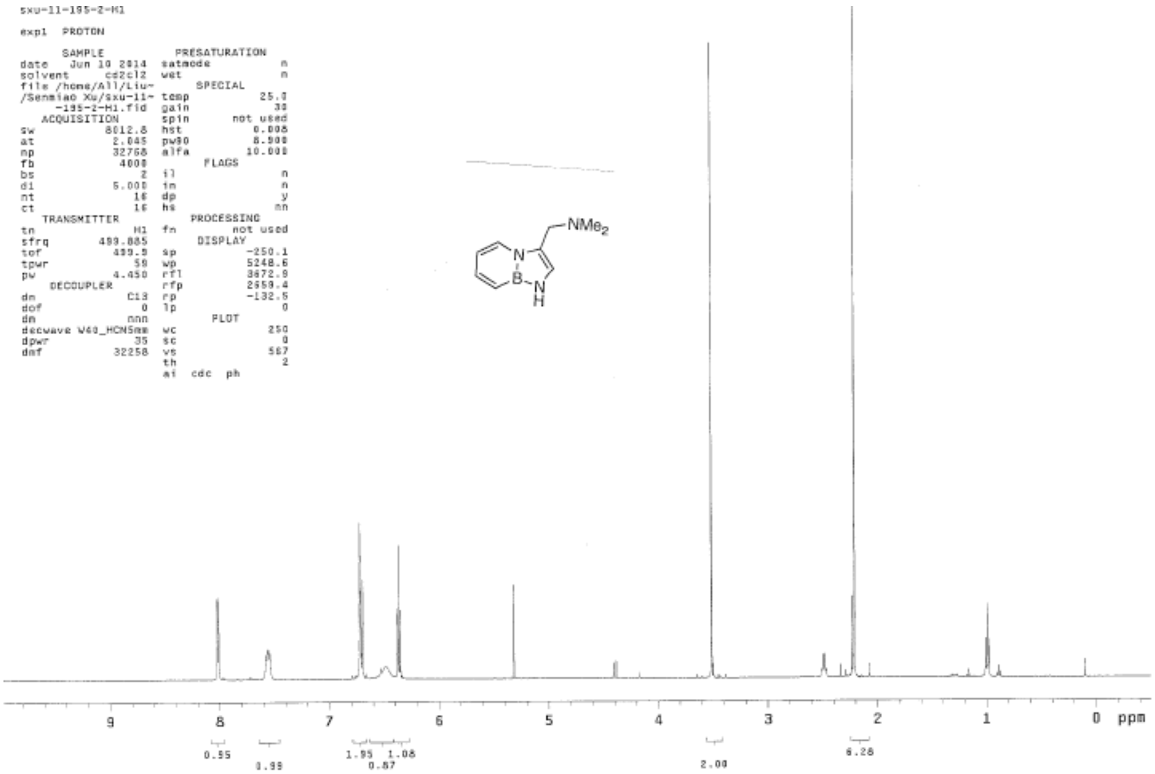
NMR Spectra



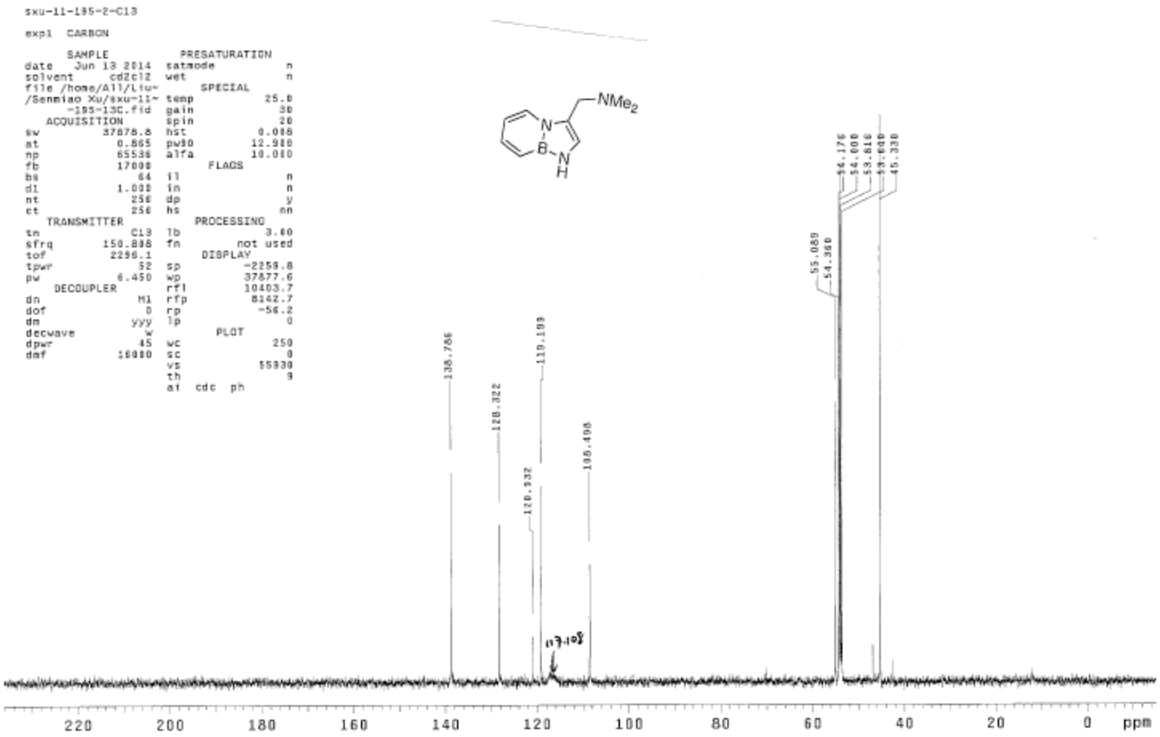
```
sxu-11-195-5-H1

exp1  PROTON

      SAMPLE            PRESATURATION
date   Jun 21 2014  satmode            n
solvent     cd2cl2  wet                n
file /home/All/Liu~         SPECIAL
/Senmiao Xu/sxu-11~ temp            25.0
    -195-5-H1.fid   gain              30
   ACQUISITION      spin        not used
sw          8012.8  hst            0.008
at           2.045  pw90           8.900
np           32768  alfa          10.000
fb            4000          FLAGS
bs               2  il                 n
d1           5.000  in                 n
nt              16  dp                 y
ct              16  hs                nn
   TRANSMITTER            PROCESSING
tn              H1  fn          not used
sfrq       499.885          DISPLAY
tof          499.9  sp            -250.1
tpwr            59  wp            5248.6
pw           4.450  rfl           3398.0
    DECOUPLER       rfp           2659.4
dn             C13  rp            -132.2
dof              0  lp                 0
dm             nnn          PLOT
decwave W40_HCN5mm  wc               250
dpwr            35  sc                 0
dmf          32258  vs               299
                    th                21
                    ai  cdc  ph
```



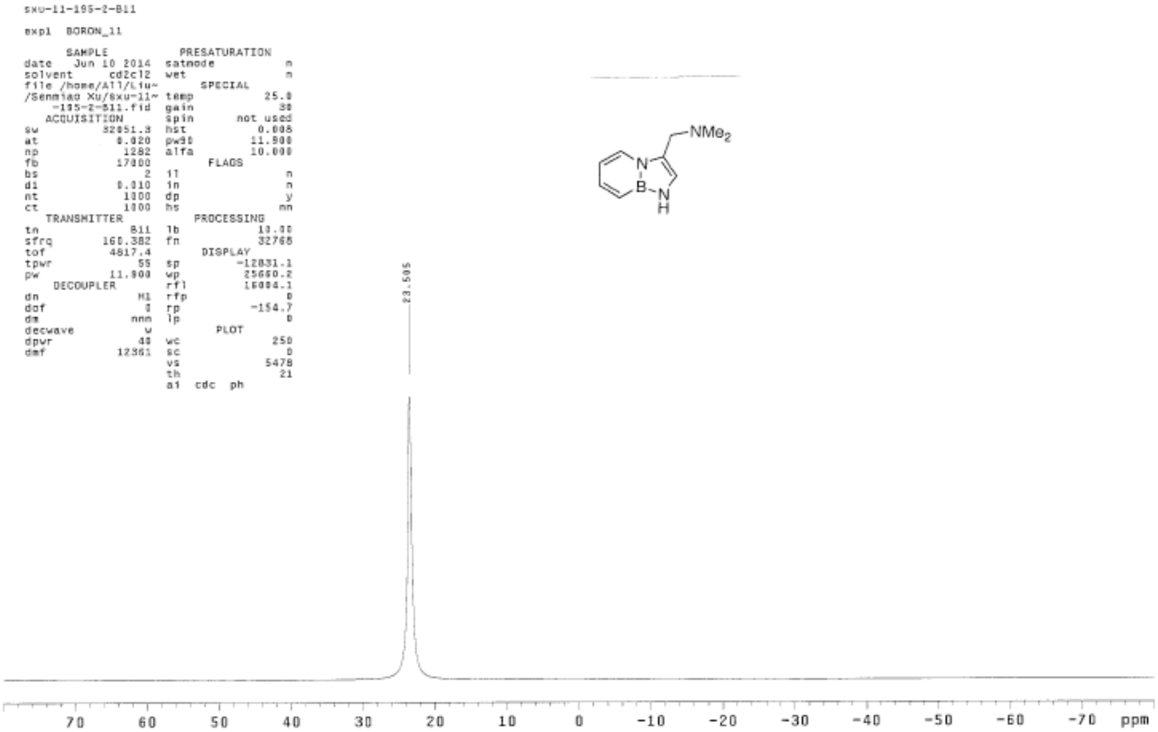
```
sxu-11-195-5-B11

exp1  BORON_11

      SAMPLE            PRESATURATION
date   Jun 21 2014  satmode            n
solvent     cd2cl2  wet                n
file /home/All/Liu~         SPECIAL
/Senmiao Xu/sxu-11~ temp            25.0
   -195-5-B11.fid   gain              30
   ACQUISITION      spin        not used
sw         32051.3  hst            0.008
at           0.020  pw90          11.900
np            1282  alfa          10.000
fb           17000          FLAGS
bs               2  il                 n
d1           0.010  in                 n
nt            1000  dp                 y
ct            1000  hs                nn
   TRANSMITTER            PROCESSING
tn             B11  lb             10.00
sfrq       160.382  fn             32768
tof         4817.4          DISPLAY
tpwr            55  sp          -12831.1
pw          11.900  wp           25660.2
    DECOUPLER       rfl          15998.3
dn              H1  rfp                0
dof              0  rp            -153.3
dm             nnn  lp                 0
decwave          w          PLOT
dpwr            40  wc               250
dmf          12361  sc                 0
                    vs              9004
                    th                15
                    ai  cdc  ph
```



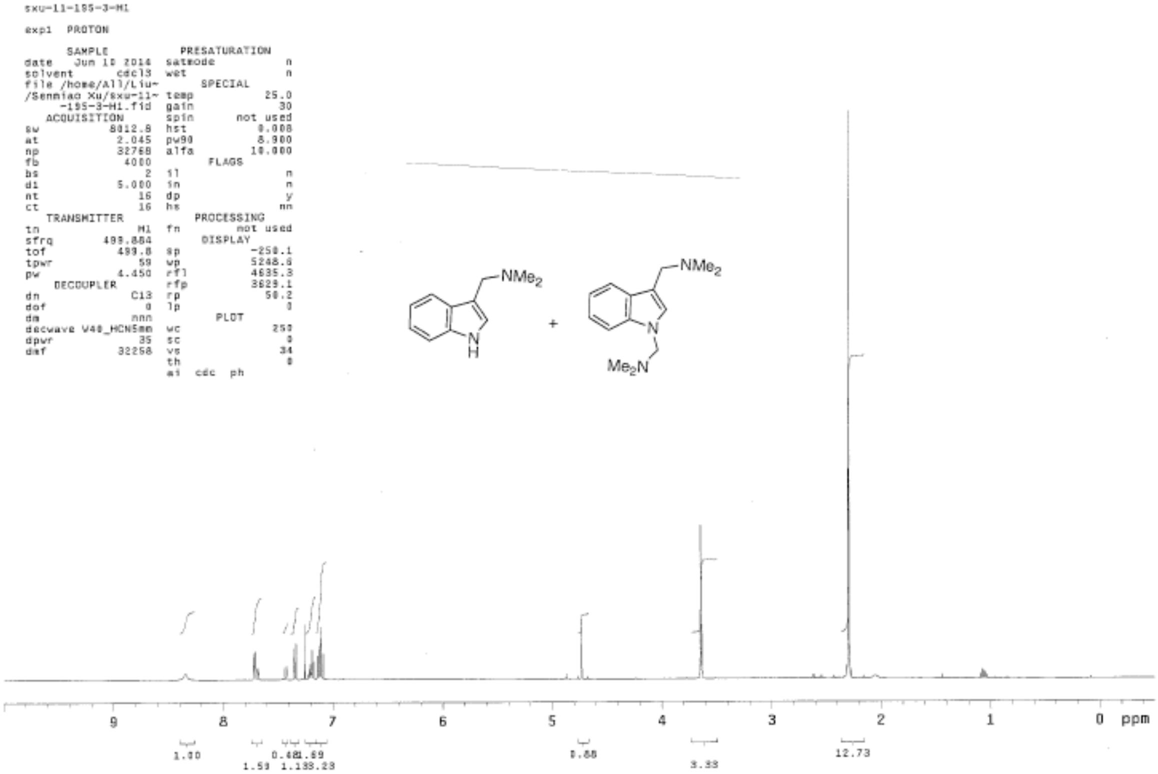
```
sxu-11-195-2-H1

exp1  PROTON

      SAMPLE              PRESATURATION
date    Jun 10 2014   satmode            n
solvent      cd2cl2   wet                n
file /home/All/Liu~          SPECIAL
/Senmiao Xu/sxu-11~   temp            25.0
     -195-2-H1.fid    gain              30
   ACQUISITION        spin        not used
sw           8012.8   hst            0.008
at            2.045   pw90           8.900
np            32768   alfa          10.000
fb             4000           FLAGS
bs                2   il                 n
d1            5.000   in                 n
nt               16   dp                 y
ct               16   hs                nn
   TRANSMITTER              PROCESSING
tn               H1   fn          not used
sfrq        499.885          DISPLAY
tof           499.5   sp            -250.1
tpwr             59   wp            5248.6
pw            4.450   rfl           3672.9
    DECOUPLER         rfp           2659.4
dn              C13   rp            -132.5
dof               0   lp                 0
dm              nnn            PLOT
decwave W40_HCN5mm    wc               250
dpwr             35   sc                 0
dmf           32258   vs               567
                      th                 2
                      ai   cdc   ph
```



```
sxu-11-195-2-C13

exp1  CARBON

      SAMPLE              PRESATURATION
date    Jun 13 2014   satmode            n
solvent      cd2cl2   wet                n
file /home/All/Liu~          SPECIAL
/Senmiao Xu/sxu-11~   temp            25.0
      -195-13C.fid    gain              30
   ACQUISITION        spin              20
sw          37878.8   hst            0.008
at            0.865   pw90          12.900
np            65536   alfa          10.000
fb            17000           FLAGS
bs               64   il                 n
d1            1.000   in                 n
nt              256   dp                 y
ct              256   hs                nn
   TRANSMITTER              PROCESSING
tn              C13   lb              3.00
sfrq        150.808   fn          not used
tof          2296.1          DISPLAY
tpwr             52   sp           -2259.8
pw            6.450   wp           37877.6
    DECOUPLER         rfl          10403.7
dn               H1   rfp           8142.7
dof               0   rp             -56.2
dm              yyy   lp                 0
decwave           w            PLOT
dpwr             45   wc               250
dmf           16000   sc                 0
                      vs             55930
                      th                 9
                      ai   cdc   ph
```



```
sxu-11-195-2-B11

exp1  BORON_11

      SAMPLE            PRESATURATION
date   Jun 10 2014  satmode            n
solvent     cd2cl2  wet                n
file /home/All/Liu~       SPECIAL
/Senmiao Xu/sxu-11~ temp            25.0
    -195-2-B11.fid  gain              30
   ACQUISITION      spin        not used
sw         32051.3  hst            0.008
at           0.020  pw90          11.900
np            1282  alfa          10.000
fb           17000          FLAGS
bs               2  il                 n
d1           0.010  in                 n
nt            1000  dp                 y
ct            1000  hs                nn
   TRANSMITTER          PROCESSING
tn             B11  lb             10.00
sfrq       160.382  fn             32768
tof         4817.4         DISPLAY
tpwr            55  sp          -12831.1
pw          11.900  wp           25660.2
    DECOUPLER       rfl          16004.1
dn              H1  rfp                0
dof              0  rp            -154.7
dm             nnn  lp                 0
decwave          w           PLOT
dpwr            40  wc               250
dmf          12361  sc                 0
                    vs              5478
                    th                21
                    ai  cdc  ph
```



```
sxu-11-195-3-H1

exp1  PROTON

      SAMPLE            PRESATURATION
date   Jun 10 2014  satmode            n
solvent      cdcl3  wet                n
file /home/All/Liu~       SPECIAL
/Senmiao Xu/sxu-11~ temp            25.0
    -195-3-H1.fid   gain              30
   ACQUISITION      spin        not used
sw          8012.8  hst            0.008
at           2.045  pw90           8.900
np           32768  alfa          10.000
fb            4000          FLAGS
bs               2  il                 n
d1           5.000  in                 n
nt              16  dp                 y
ct              16  hs                nn
   TRANSMITTER          PROCESSING
tn              H1  fn          not used
sfrq       499.884         DISPLAY
tof          499.8  sp            -250.1
tpwr            59  wp            5248.6
pw           4.450  rfl           4635.3
    DECOUPLER       rfp           3829.1
dn             C13  rp              50.2
dof              0  lp                 0
dm             nnn           PLOT
decwave W40_HCN5mm  wc               250
dpwr            35  sc                 0
dmf          32258  vs                34
                    th                 0
                    ai  cdc  ph
```