

# Triangular boron carbon nitrides: An unexplored family of chromophores with unique properties for photocatalysis and optoelectronics

## Electronic Supporting Information

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### Section S1: Additional data for the compounds of Chart 1

Table S1: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) of **1.1**.

Singlet		Triplet	
$A_2'$	1.02 (0.000)	$A_2'$	1.18
$E'$	3.14 (0.520)	$E'$	2.25
$A_1''$	4.84 (0.000)	$E'$	4.27
$E'$	5.07 (0.768)	$A_1''$	4.84

Table S2: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) of **2.1**.

Singlet		Triplet	
$A_2'$	1.63 (0.000)	$E'$	1.91
$A_1'$	2.25 (0.000)	$A_1'$	1.93
$E'$	2.37 (0.586)	$A_2'$	1.94
$E'$	3.16 (0.110)	$E'$	2.88

Table S3: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) of **3.1**.

Singlet		Triplet	
$A_2'$	1.19 (0.000)	$A_2'$	1.42
$E'$	2.27 (1.262)	$E'$	1.89
$E'$	2.51 (0.000)	$E'$	2.36
$A_2'$	2.91 (0.000)	$E'$	2.51
$A_1'$	3.08 (0.000)	$A_1'$	2.78

## Section S2: Additional data for the compounds of Chart 2

Table S4: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) of **1.2**.

Singlet		Triplet	
$A_2'$	2.57 (0.000)	$A_2'$	2.85
$A_1''$	3.76 (0.000)	$E'$	3.67
$E''$	3.84 (0.000)	$A_1''$	3.76
$E'$	4.43 (0.538)	$E''$	3.82

Table S5: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) of **2.2**.

Singlet		Triplet	
$A_2'$	2.22 (0.000)	$A_2'$	2.57
$E'$	2.98 (0.446)	$E'$	2.67
$A_1'$	3.21 (0.000)	$A_1'$	2.99
$A_1''$	3.92 (0.000)	$E'$	3.49

Table S6: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) of **3.2**.

Singlet		Triplet	
$A_2'$	1.91 (0.000)	$A_2'$	2.22
$E'$	2.69 (0.966)	$E'$	2.36
$E'$	3.14 (0.077)	$E'$	2.92
$A_2'$	3.24 (0.000)	$E'$	3.02
$E'$	3.40 (1.177)	$A_1'$	3.12

### Section S3: Molecular orbitals of Hz, Nz and Dz

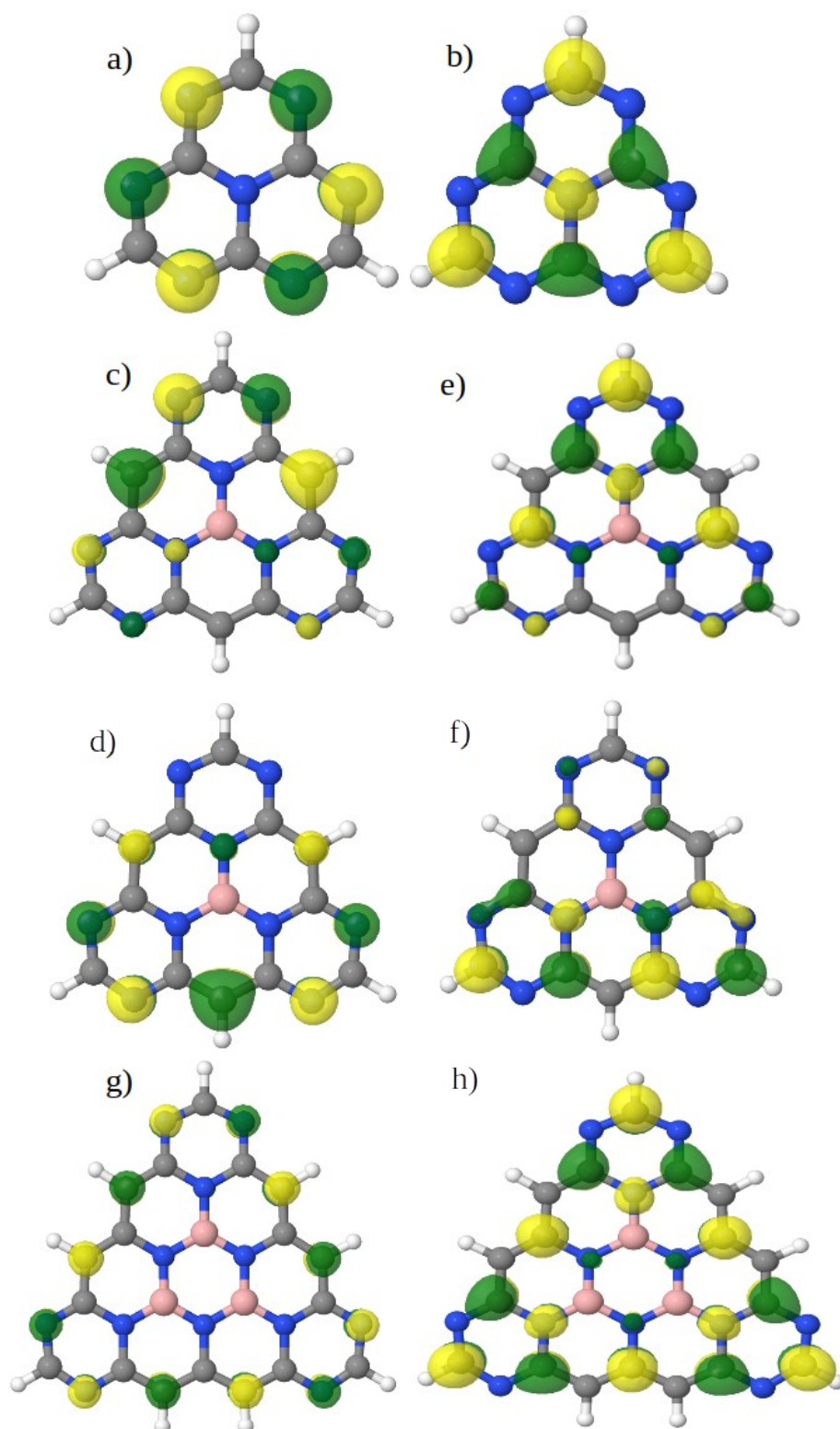


Figure S1: HOMO and LUMO of the molecules **1.2** (a and b), **2.2** (c, d and e, f) and **3.2** (g and h), respectively, at their ground-state equilibrium structures.

### Section S4: Selected asymmetrically CH → N substituted derivatives of 3.1

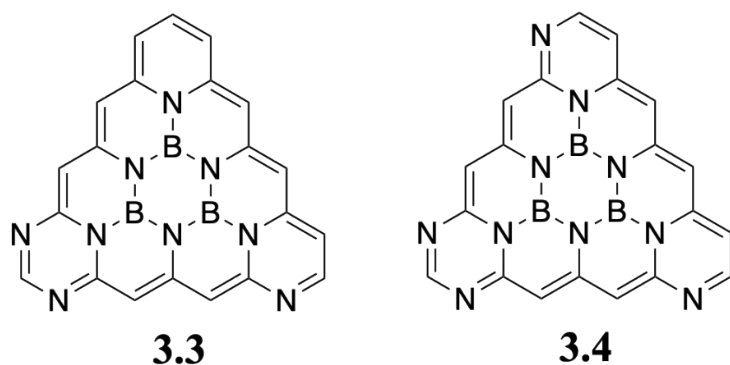


Chart S1: Selected asymmetrically CH → N substituted derivatives of 3.1.

Table S7: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) for two selected asymmetrically CH → N substituted derivatives of 3.1. The corresponding structures are shown in Chart S1.

State	<b>3.3</b>	<b>3.4</b>
$S_1 A'$	1.63 (0.020)	1.68 (0.010)
$S_2 A'$	2.46 (0.429)	2.44 (0.350)
$S_3 A'$	2.65 (0.645)	2.63 (0.646)
$S_4 A'$	2.80 (0.084)	2.92 (0.201)
$T_1 A'$	1.79	1.93
$T_2 A'$	2.13	2.19
$T_3 A'$	2.22	2.26
$T_4 A'$	2.63	2.63

## Section S5: Additional selected fluorinated derivatives of nonazine

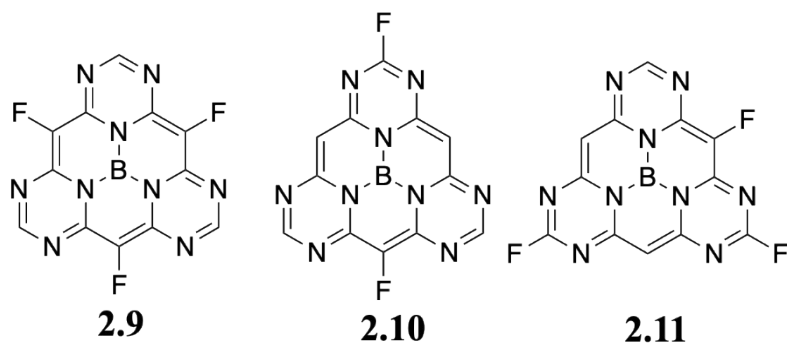


Chart S2: Selected fluorinated derivatives of Nz (**2.2**).

Table S8: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) for selected fluorinated derivatives of Nz (**2.2**). **2.9** exhibits the lowest  $S_1$  energy, while **2.10** and **2.11** exhibit the highest oscillator strength of the  $S_1$  state. The corresponding structures are shown in Chart S2.

State	<b>2.9</b>	<b>2.10</b>	<b>2.11</b>
$S_1 A'$	1.86 (0.000)	2.14 (0.022)	2.26 (0.022)
$S_2 A'$	2.61 (0.350)	2.92 (0.199)	3.06 (0.168)
$S_3 A'$	-	3.07 (0.162)	3.14 (0.189)
$S_4 A'$	2.80 (0.000)	3.20 (0.011)	3.33 (0.016)
$T_1 A'$	2.18	2.29	2.41
$T_2 A'$	2.27	2.64	2.75
$T_3 A'$	-	2.82	2.90
$T_4 A'$	3.14	2.97	3.10

## Section S6: Selected fluorinated derivatives of dodecazine

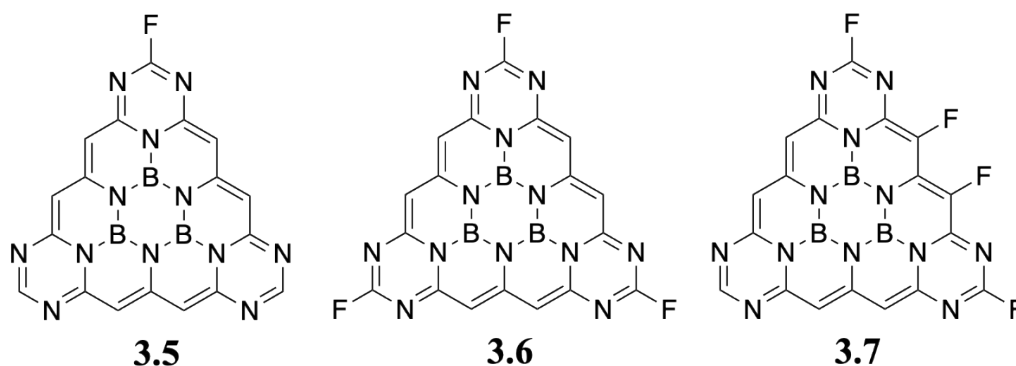


Chart S3: Selected fluorinated derivatives of Dz (**3.2**).

Table S9: Vertical excitation energies (in eV) and oscillator strengths (in parentheses) for selected fluorinated derivatives of Dz (**3.2**). The corresponding structures are shown in Chart S3.

State	Symmetry	<b>3.5</b>	Symmetry	<b>3.6</b>	Symmetry	<b>3.7</b>
$S_1$	B <sub>2</sub>	1.98 (0.006)	A <sub>2</sub> '	2.17 (0.000)	B <sub>2</sub>	1.91 (0.015)
$S_2$	A <sub>1</sub>	2.70 (0.468)	E'	2.93 (1.040)	B <sub>2</sub>	2.60 (0.547)
$S_3$	B <sub>2</sub>	2.85 (0.514)		-	A <sub>1</sub>	2.79 (0.326)
$S_4$	A <sub>1</sub>	3.17 (0.017)	E'	3.35 (0.252)	B <sub>2</sub>	2.96 (0.003)
$T_1$	B <sub>2</sub>	2.27	A <sub>2</sub> '	2.48	B <sub>2</sub>	1.98
$T_2$	A <sub>1</sub>	2.39	E'	2.50	B <sub>2</sub>	2.32
$T_3$	B <sub>2</sub>	2.45		-	B <sub>2</sub>	2.79
$T_4$	A <sub>1</sub>	2.94	E'	3.12	B <sub>2</sub>	2.95

### Section S7: Jahn-Teller-Effect in the <sup>3</sup>E' state of **2.1** and **2.2**

The JT effect in the <sup>3</sup>E' state as well as PJT interactions among the <sup>3</sup>A<sub>1</sub>', <sup>3</sup>A<sub>2</sub>' and <sup>3</sup>E' states arising from excitation from the degenerate HOMO to the degenerate LUMO remove the degeneracy of the <sup>3</sup>E' state and lead to a stabilization of the lower adiabatic potential energy. The components E<sub>x</sub> and E<sub>y</sub> of the E' state transform as the B<sub>1</sub> and A<sub>1</sub> representations in C<sub>2v</sub> symmetry, respectively. The minimum of the A<sub>1</sub> surface represents the minimum of the (P)JT distorted surface of the E' state. The B<sub>1</sub> surface exhibits a stationary point which represents the saddle point for the so-called pseudorotation. The difference between the vertical excitation energy of the E' state and the minimum of the A<sub>1</sub> state is the (P)JT stabilization energy.

The excitation energies from the electronic ground state to the minima and saddle points of the <sup>3</sup>E' surface (adiabatic excitation energies) are listed in Tables S10 and S11 for **2.1** and **2.2**, respectively. The energies for vertical emission from the excited-state stationary points to the electronic ground state (vertical emission energies) are also listed in Tables S10 and S11.

A schematic representation of the potential-energy surfaces of the <sup>1</sup>A<sub>2</sub>', <sup>3</sup>A<sub>2</sub>' and <sup>3</sup>E' states of **2.1** and **2.2** is given by Fig. S2. For clarity, only the lower component of the <sup>3</sup>E' surface is shown. For **2.1**, the (P)JT coupling reduces the vertical S<sub>1</sub>-T<sub>1</sub> gap of - 0.28 eV to an adiabatic S<sub>1</sub>-T<sub>1</sub> gap of merely - 0.02 eV. For **2.2**, the (P)JT coupling reduces the vertical S<sub>1</sub>-T<sub>1</sub> gap of - 0.35 eV to an adiabatic S<sub>1</sub>-T<sub>1</sub> gap of - 0.28 eV.

It can be seen in Tables S10 and S11 and in Fig. S2 that for the nondegenerate states (<sup>1</sup>A<sub>2</sub>', <sup>3</sup>A<sub>2</sub>') the difference between the adiabatic excitation energies and the vertical emission energies is very small, which reflects the unusual rigidity of the BCNs in nondegenerate excited states.

Table S10: Adiabatic excitation energies ( $E_a$ ), vertical emission energies ( $E_{em}$ ) (in eV) and leading electronic configurations of the lowest excited states of **2.1** calculated with the ADC(2)/cc-pVDZ method at the respective ADC(2)-optimized geometries.

State	$E_a$	$E_{em}$	electronic configuration
<sup>1</sup> A <sub>2</sub> '	1.59	1.58	0.70(5a <sub>2</sub> -8b <sub>2</sub> )+0.70(7b <sub>2</sub> -6a <sub>2</sub> )
<sup>3</sup> E <sub>y</sub> ( <sup>3</sup> A <sub>1</sub> )	1.61	1.27	0.98(5a <sub>2</sub> -6a <sub>2</sub> )
<sup>3</sup> E <sub>x</sub> ( <sup>3</sup> B <sub>1</sub> )	1.85	1.80	0.98(7b <sub>2</sub> -6a <sub>2</sub> )
<sup>3</sup> A <sub>2</sub> '	1.91	1.90	0.70(5a <sub>2</sub> -8b <sub>2</sub> )+0.70(7b <sub>2</sub> -6a <sub>2</sub> )

Table S11: Adiabatic excitation energies ( $E_a$ ), vertical emission energies ( $E_m$ ) (in eV) and leading electronic configurations of the lowest excited states of **2.2** calculated with the ADC(2)/cc-pVDZ method at the respective ADC(2)-optimized geometries.

State	$E_a$	$E_m$	electronic configuration
$^1A_2'$	2.17	2.14	$0.69(5a_2-8b_2)-0.69(7b_2-6a_2)$
$^3E_y(^3A_1)$	2.45	1.94	$0.97(7b_2-8b_2)$
$^3E_x(^3B_1)$	2.50	2.42	$0.95(5a_2-8b_2)$
$^3A_2'$	2.52	2.49	$0.70(5a_2-8b_2)-0.70(7b_2-6a_2)$

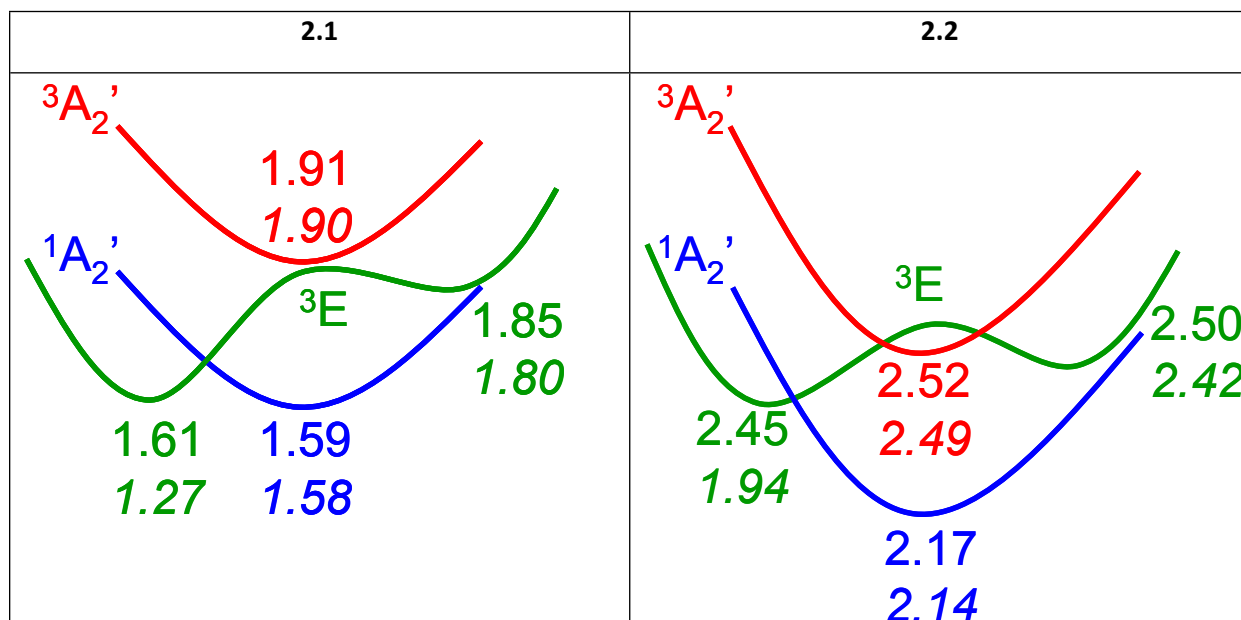


Figure S2: Schematic representation of the potential-energy surfaces of the  $^1A_2'$ ,  $^3A_2'$  and  $^3E'$  states of compounds **2.1** and **2.2**. Adiabatic excitation energies are given by roman fonts; vertical emission energies are given by italic fonts (see Tables S10 and S11).

## Section S8: Cartesian coordinates

Cartesian coordinates in Angstrom of Cz (**1.1**) at the MP2/cc-pVDZ level.

C	-2.1261712	-1.2025280	0.0000000
C	-0.7073599	-1.2251833	0.0000000
N	0.0000000	0.0000000	0.0000000
C	-0.7073599	1.2251833	0.0000000
C	-2.1261712	1.2025280	0.0000000
C	-2.8275277	0.0000000	0.0000000
C	1.4147198	0.0000000	0.0000000
C	2.1045054	1.2400543	0.0000000
C	1.4137639	2.4487108	0.0000000
C	0.0216658	2.4425823	0.0000000
C	0.0216658	-2.4425823	0.0000000
C	1.4137639	-2.4487108	0.0000000
C	2.1045054	-1.2400543	0.0000000
H	-2.6372860	2.1682456	0.0000000
H	-0.5591128	3.3680794	0.0000000
H	3.1963988	1.1998339	0.0000000
H	3.1963988	-1.1998339	0.0000000
H	-0.5591128	-3.3680794	0.0000000
H	-2.6372860	-2.1682456	0.0000000
H	-3.9229787	0.0000000	0.0000000
H	1.9614894	-3.3973992	0.0000000
H	1.9614894	3.3973992	0.0000000



Cartesian coordinates in Angstrom of Hz (**1.2**) at the MP2/cc-pVDZ level.

N	-2.3770694	0.0167866	0.0000000
C	-1.2302088	-0.6816424	0.0000000
N	-0.0000035	0.0000018	0.0000000
C	0.0247821	1.4061780	0.0000000
N	-1.1300922	2.0913252	0.0000000
C	-2.2459412	1.3500242	0.0000000
C	1.2054004	-0.7245397	0.0000000
N	2.3761902	-0.0669661	0.0000000
C	2.2921121	1.2700625	0.0000000
N	1.2030653	2.0502198	0.0000000
N	-1.2460863	-2.0243537	0.0000000
C	-0.0461543	-2.6200497	0.0000000
N	1.1740040	-2.0669785	0.0000000
H	-3.1857918	1.9149024	0.0000000
H	-0.0655010	-3.7164210	0.0000000
H	3.2512947	1.8014504	0.0000000

Cartesian coordinates in Angstrom of **2.1** at the MP2/cc-pVDZ level.

C	-0.7292978	3.6862196	0.0000000
C	-0.0040452	2.4749592	0.0000000
N	-0.7261856	1.2577904	0.0000000
C	-2.1413550	1.2409829	0.0000000
C	-2.8277109	2.4747002	0.0000000
C	-2.1263455	3.6829384	0.0000000
C	-2.7962504	0.0000000	0.0000000
C	-2.1413550	-1.2409829	0.0000000
N	-0.7261856	-1.2577904	0.0000000
C	-0.0040452	-2.4749592	0.0000000
C	-0.7292978	-3.6862196	0.0000000
C	-2.1263455	-3.6829384	0.0000000
C	-2.8277109	-2.4747002	0.0000000
C	1.3981252	-2.4216239	0.0000000

C	2.1454002	-1.2339764	0.0000000
N	1.4523712	0.0000000	0.0000000
C	2.1454002	1.2339764	0.0000000
C	3.5570087	1.2115194	0.0000000
C	4.2526910	0.0000000	0.0000000
C	3.5570087	-1.2115194	0.0000000
B	0.0000000	0.0000000	0.0000000
C	1.3981252	2.4216239	0.0000000
H	-2.6741502	-4.6317640	0.0000000
H	-3.8889339	0.0000000	0.0000000
H	-2.6741502	4.6317640	0.0000000
H	1.9444670	3.3679156	0.0000000
H	1.9444670	-3.3679156	0.0000000
H	5.3483004	0.0000000	0.0000000
H	-3.9207361	-2.4500906	0.0000000
H	-3.9207361	2.4500906	0.0000000
H	-0.1614726	4.6205024	0.0000000
H	4.0822088	2.1704118	0.0000000
H	4.0822088	-2.1704118	0.0000000
H	-0.1614726	-4.6205024	0.0000000

Cartesian coordinates in Angstrom of Nz(2.2) at the MP2/cc-pVDZ level.

N	3.4842312	1.2145238	0.0000000
C	2.1335374	1.2174790	0.0000000
N	1.4327146	0.0000000	0.0000000
C	2.1335374	-1.2174790	0.0000000
N	3.4842312	-1.2145238	0.0000000
C	4.0562904	0.0000000	0.0000000
C	1.3918435	-2.4107437	0.0000000
C	-0.0124010	-2.4564371	0.0000000
N	-0.7163573	-1.2407672	0.0000000
B	0.0000000	0.0000000	0.0000000
C	1.3918435	2.4107437	0.0000000
C	-0.0124010	2.4564371	0.0000000

N	-0.7163573	1.2407672	0.0000000
N	-0.6903071	-3.6246947	0.0000000
H	5.1533873	0.0000000	0.0000000
N	-0.6903071	3.6246947	0.0000000
C	-2.1211364	-1.2389581	0.0000000
C	-2.1211364	1.2389581	0.0000000
C	-2.0281452	3.5128505	0.0000000
C	-2.0281452	-3.5128505	0.0000000
N	-2.7939241	2.4101709	0.0000000
N	-2.7939241	-2.4101709	0.0000000
C	-2.7836870	0.0000000	0.0000000
H	1.9368801	-3.3547748	0.0000000
H	-2.5766936	-4.4629643	0.0000000
H	-3.8737602	0.0000000	0.0000000
H	1.9368801	3.3547748	0.0000000
H	-2.5766936	4.4629643	0.0000000

Cartesian coordinates in Angstrom of **3.1** at the MP2/cc-pVDZ level.

C	-1.2143575	0.0000000	4.9822765
C	-1.2349458	0.0000000	3.5690907
N	0.0000000	0.0000000	2.8873311
C	1.2349458	0.0000000	3.5690907
C	1.2143575	0.0000000	4.9822765
C	0.0000000	0.0000000	5.6737176
C	-2.4269998	0.0000000	2.8193792
C	-2.4782067	0.0000000	1.4179996
C	-3.6662591	0.0000000	0.6729879
C	-3.7195022	0.0000000	-0.7341992
N	-2.5115608	0.0000000	-1.4627794
C	-2.4844906	0.0000000	-2.8731675
C	-3.7186463	0.0000000	-3.5619464
C	-4.9246499	0.0000000	-2.8560505
C	-4.9330330	0.0000000	-1.4586714
B	-1.2527563	0.0000000	-0.7360746

N	-1.2497769	0.0000000	0.7087960
B	0.0000000	0.0000000	1.4337763
N	1.2497769	0.0000000	0.7087960
C	2.4782067	0.0000000	1.4179996
C	3.6662591	0.0000000	0.6729879
C	3.7195022	0.0000000	-0.7341992
N	2.5115608	0.0000000	-1.4627794
C	2.4844906	0.0000000	-2.8731675
C	3.7186463	0.0000000	-3.5619464
C	4.9246499	0.0000000	-2.8560505
C	4.9330330	0.0000000	-1.4586714
B	1.2527563	0.0000000	-0.7360746
N	0.0000000	0.0000000	-1.4559217
C	0.0000000	0.0000000	-2.8743701
C	-1.2392465	0.0000000	-3.5307117
C	1.2392465	0.0000000	-3.5307117
C	2.4269998	0.0000000	2.8193792
H	0.0000000	0.0000000	6.7696094
H	-5.8736764	0.0000000	-3.4040513
H	5.8736764	0.0000000	-3.4040513
H	-4.6164788	0.0000000	1.2130589
H	-3.3697978	0.0000000	3.3723073
H	3.3697978	0.0000000	3.3723073
H	4.6164788	0.0000000	1.2130589
H	-1.2467256	0.0000000	-4.6236588
H	1.2467256	0.0000000	-4.6236588
H	-3.6973354	0.0000000	-4.6547666
H	3.6973354	0.0000000	-4.6547666
H	-5.8687629	0.0000000	-0.8937602
H	5.8687629	0.0000000	-0.8937602
H	2.1713971	0.0000000	5.5102593
H	-2.1713971	0.0000000	5.5102593

Cartesian coordinates in Angstrom of Dz (3.2) at the MP2/cc-pVDZ level.

B	-0.7169416	1.2417793	0.0000000
N	-1.4439754	0.0000000	0.0000000
B	-0.7169416	-1.2417793	0.0000000
N	0.7219877	-1.2505193	0.0000000
B	1.4338832	0.0000000	0.0000000
N	0.7219877	1.2505193	0.0000000
N	2.8682226	0.0000000	0.0000000
N	-1.4341113	2.4839536	0.0000000
N	-1.4341113	-2.4839536	0.0000000
C	1.4275984	2.4726730	0.0000000
C	1.4275984	-2.4726730	0.0000000
C	-2.8551968	0.0000000	0.0000000
C	-2.8401170	2.4816614	0.0000000
C	-0.7291233	3.7004441	0.0000000
C	3.5692403	1.2187828	0.0000000
C	3.5692403	-1.2187828	0.0000000
C	-2.8401170	-2.4816614	0.0000000
C	-0.7291233	-3.7004441	0.0000000
N	-1.4084135	4.8701842	0.0000000
N	-3.5134965	3.6548140	0.0000000
C	-2.7463162	4.7567593	0.0000000
N	4.9219100	-1.2153703	0.0000000
N	4.9219100	1.2153703	0.0000000
C	5.4926325	0.0000000	0.0000000
N	-1.4084135	-4.8701842	0.0000000
N	-3.5134965	-3.6548140	0.0000000
C	-2.7463162	-4.7567593	0.0000000
C	0.6750714	3.6646625	0.0000000
C	2.8361552	2.4169602	0.0000000
C	0.6750714	-3.6646625	0.0000000
C	2.8361552	-2.4169602	0.0000000
C	-3.5112265	-1.2477023	0.0000000

C	-3.5112265	1.2477023	0.0000000
H	-3.2950197	5.7071415	0.0000000
H	6.5900394	0.0000000	0.0000000
H	-3.2950197	-5.7071415	0.0000000
H	3.4152579	3.3420343	0.0000000
H	1.1866576	4.6287172	0.0000000
H	-4.6019155	1.2866830	0.0000000
H	-4.6019155	-1.2866830	0.0000000
H	3.4152579	-3.3420343	0.0000000
H	1.1866576	-4.6287172	0.0000000