Supporting Information

Photoreactions of Phenylborylene with Dinitrogen and Carbon Monoxide

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1. UV/vis spectrum of diazdiophenylborane (2)



Figure S1. UV/vis spectrum of diazide **2** in a dinitrogen matrix at 28 K.

2. Computed Geometry of PhNB(NCO)





Figure S2. Structure of PhNB(NCO) in $C_{2\nu}$ symmetry computed at the B3LYP/6-311+G** level of theory. The structure of (isocyanato)dimethylborane (in C_1) is given for comparison. Important bond lengths are given in Å.

3. ESR spectra obtained from 350-450 nm irradiation



Figure S3. ESR spectra (N₂, 15 K) obtained after irradiation of **2**. a) Increase of the small *D* signal due 350 nm $< \lambda < 450$ nm irradiation; black: $\lambda = 254$ nm/30min; blue: 350 nm $< \lambda < 450$ nm, 10 min; red: 350 nm $< \lambda 450$ nm, additional 20 min. b) Decrease of the small *D* signal due to 308-nm-irradiation: red: identical to red trace in a.

4. IR Spectroscopic Data and Comparison with Computational Results

Table S1. Experimental and computed $(B3LYP/6-311+G^{**})$ vibrational frequencies of PhNBNCO (5), computed intensities (in km mol⁻¹), and the corresponding isotopic shifts.

P	h-NB-NC	0	Ph-NB-N ¹³ CO		Ph-N	B-NC ¹⁸ O	
v_{exp} [cm ⁻¹]	ω_{theor} [cm ⁻¹]	Intensity	v_{exp} [cm ⁻¹]	ω_{theor} [cm ⁻¹]	v_{exp} [cm ⁻¹]	ω_{theor} [cm ⁻¹]	Assignment
2315-	2441.9	2968.5	2255-2272	2378.5	2299-	2428.3	v(NCO)
2332					2316		
2081.2	2125.2	1055.2	2080.6	2123.8	2079.7	2123.9	$\nu(BN)$
2131	2184.6		2131	2182.6	2126	2183.1	$v(^{10}BN)$
594/596	594.7	25.2	577/579	577.5	588/590	589.3	δ(NCO)
~ 605	589.1	26.1	~ 589	572.1	~ 600	583.7	δ(NCO)
			Δv_{exp} [cm ⁻¹]	$\Delta\omega_{ m theor}$ [cm ⁻¹]	Δv _{exp} [cm ⁻¹]	$\Delta \omega_{\text{theor}}$ [cm ⁻¹]	
			60	63.4	16	13.6	v(NCO)
			0.6	1.4	1.5	1.3	$\nu(BN)$
			0	2.0	5	1.5	$v(^{10}BN)$
			17	17.2	6	5.4	δ(NCO)
			~ 16	17.0	~ 5	5.4	δ(NCO)

Table S2. Experimental and computed $(B3LYP/6-311+G^{**})$ vibrational frequencies of PhB(CO) (7), computed intensities (in km mol⁻¹), and the corresponding isotopic shifts.

	PhB(CO)			PhB(¹³ CO)		C ¹⁸ O)	
v_{exp} [cm ⁻¹]	ω_{theor} [cm ⁻¹]	Intensity	v_{exp} [cm ⁻¹]	ω _{theor} [cm ⁻¹]	v_{exp} [cm ⁻¹]	ω _{theor} [cm ⁻¹]	Assignment
2012/2006	2058.8	781.8	1961/1956	2006.0	1986/1981	2032.7	v(BCO)
1402	1432.9	168.2	1402	1432.5	1393ª	1421.2	δ(in-plane)/ v(BCO)
			Δv _{exp} [cm ⁻¹]	$\Delta \omega_{ m theor}$ [cm ⁻¹]	Δv _{exp} [cm ⁻¹]	$\Delta \omega_{\text{theor}}$ [cm ⁻¹]	
			51/50	52.8	26/25	26.1	v(BCO)
			0	0.4	9	11.7	δ(in-plane)/ v(BCO)

^a Tentative assignment due to overlap with signals of PhB(NN).

Table S3. Experimental and computed $(B3LYP/6-311+G^{**})$ vibrational frequencies of PhB(NN) (6), computed intensities (in km mol⁻¹), and the corresponding isotopic shifts.

	Ph-BNN			Ph-B ¹	⁵ (N) ₂		
v_{exp} [cm ⁻¹]	ω_{theor} [cm ⁻¹]	Intensity	v_{exp} [cm ⁻¹]	ω_{theor} [cm ⁻¹]	Δv _{exp} [cm ⁻¹]	$\Delta\omega_{ m theor}$ [cm ⁻¹]	Assignment
1691	1752.8	108.5		1724.0		28.8	v(BNN)
1417-1387	1433.0	286.1	1373-1367	1408.1	~ 25-28	24.9	δ(in-plane)/ v(BNN)

Table S4. Computed $(B3LYP/6-311+G^{**})$ vibrational frequencies of PhB(CO)₂, computed intensities (in km mol⁻¹), and the corresponding isotopic shifts.

PhB	B(CO)2	PhB(¹³ CO) ₂		PhB(C	¹⁸ O)2	
ω _{theor} [cm ⁻¹]	Intensity	$\omega_{ m theor}$ [cm ⁻¹]	$\Delta \omega_{ m theor}$ [cm ⁻¹]	$\omega_{ m theor}$ [cm ⁻¹]	$\Delta \omega_{\text{theor}}$ [cm ⁻¹]	Assignment
2175.2	489.3	2120.4	54.8	2133.5	41.7	v _{sym} (CO)
2069.0	1573.1	2017.7	51.3	2029.3	39.7	$v_{asym}(CO)$

5. Computed excited state energies

Table S5. Excited states symmetries, energies (eV), absorption wavelengths (nm), and oscillator strengths computed for conformers of $PhB(N_3)_2$, isomers of $PhBN_2$ stoichiometry, PhB, and PhNBNCO at the TD-B3LYP/6-311+G**//B3LYP/6-311+G** level of theory. The most intensive absorptions are highlighted in green.

Compound	State	eV	nm		Compound	State	eV	nm	
C6H5B(N3)2	Singlet-B2	4.25	292	f=0.0058	C6H5BN2	Singlet-B1	2.72	456	f=0.0019
conformer1	Singlet-A1	4.47	277	f=0.4346	3ring	Singlet-A2	3.82	324	f=0.0000
N=N=N	Singlet-A2	4.62	269	f=0.0000		Singlet-A1	4.70	264	f=0.0012
К К К К К К К К К К К К К К К К К К К	Singlet-B1	4.87	254	f=0.0001	Ĭ́́́́́́́́́́́́́́́́́́́́́́́́́́́́́́́́́́	Singlet-B2	4.77	260	f=0.0014
N=N=N	Singlet-B2	4.88	254	f=0.0587		Singlet-B2	4.96	250	f=0.0231
	Singlet-A2	4.94	251	f=0.0000		Singlet-B1	5.16	240	f=0.0002
	Singlet-A2	5.15	241	f=0.0000		Singlet-A1	5.56	223	f=0.2035
	Singlet-B2	5.63	220	f=0.0034		Singlet-B2	5.97	208	f=0.0007
	Singlet-B1	5.72	217	f=0.0003		Singlet-A2	6.23	199	f=0.0000
	Singlet-A2	5.83	213	f=0.0000		Singlet-A1	6.53	190	f=0.0463
conformer2	Singlet-A'	4.41	281	f=0.0171	PhNBN, ³ A ₂		1.61	772	f=0.0000
N=N=N	Singlet-A'	4.61	269	f=0.3306			1.95	634	f=0.0921
– K −	Singlet-A'	4.97	249	f=0.1418			2.57	482	f=0.0024
N N	Singlet-A"	4.98	249	f=0.0002			2.65	468	f=0.0031
Ň	Singlet-A"	5.14	241	f=0.0000			2.71	457	f=0.0000
_	Singlet-A"	5.21	238	f=0.0005			2.79	444	f=0.0025
	Singlet-A"	5.25	236	f=0.0000			3.08	403	f=0.0000
	Singlet-A"	5.49	226	f=0.0001			3.42	362	f=0.1444
	Singlet-A"	5.59	222	f=0.0003			4.05	306	f=0.2110
	Singlet-A'	5.67	219	f=0.0057			4.33	286	f=0.0303
conformer3	Singlet-B	4.56	272	f=0.0045	PhBNN, ³ A ₂		3.13	396	f=0.0469
N	Singlet-A	4.61	269	f=0.1143			3.31	375	f=0.0000
N N	Singlet-B	4.80	258	f=0.0081			3.69	336	f=0.0001
<≻−в(_]	Singlet-B	5.06	245	f=0.2195			3.99	311	f=0.1202
	Singlet-A	5.21	238	f=0.0013			4.02	308	f=0.0087



	Singlet-B	5.33	233	f=0.0017		4.29	289	f=0.0002
	Singlet-A	5.41	229	f=0.0058		4.41	281	f=0.0000
	Singlet-B	5.51	225	f=0.0004		4.42	281	f=0.0510
	Singlet-A	5.65	219	f=0.0056		4.46	278	f=0.0000
	Singlet-B	5.71	217	f=0.0068		4.52	274	f=0.0037
C6H5B	Singlet-B1	2.34	529	f=0.0128	C6H5NBNCO Singlet-A1	4.68	265	f=0.4720
	Singlet-B2	3.16	392	f=0.0412	Singlet-A2	4.75	261	f=0.0000
	Singlet-A2	3.87	320	f=0.0000	Singlet-B2	4.84	256	f=0.0021
	Singlet-B2	4.59	270	f=0.0227	Singlet-B1	5.07	245	f=0.0023
	Singlet-A1	5.02	247	f=0.0815	Singlet-A2	5.36	231	f=0.0000
	Singlet-B1	5.10	243	f=0.0720	Singlet-B1	5.68	218	f=0.0013
	Singlet-A2	5.18	239	f=0.0000	Singlet-B2	5.75	215	f=0.1421
	Singlet-B1	5.21	238	f=0.0035	Singlet-B1	5.93	209	f=0.0003
	Singlet-A1	5.27	235	f=0.1912	Singlet-A1	5.94	209	f=0.0281
	Singlet-B2	5.59	222	f=0.0240	Singlet-A2	6.04	205	f=0.0000

6. Cartesian Coordinates

The Cartesian coordinates computed at the B3LYP/6-311+ G^{**} level of the isomers of PhBN₆,¹ PhBN₂,¹ and PhB² isomer were published in Supporting Information sections of pervious publications.

Cartesian coordinates were obtained at the B3LPY/6-311+G** level of theory and are given in Å.

12 PhNB (6 6 6 6 6 6 7 7 5 7 1 1 1 1 1 1 6 8	NCO) -479.523 0.000000 0.000000 0.000000 0.000000 0.000000	703733 00 00 00 00 00 00 00 00 00 00 00 00 0	0.0000 1.2042 1.2100 0.0000 1.2100 0.0000 0.0000 2.1465 2.1431 2.1431 2.1445 0.0000 0.0000 0.0000	00000 67000 48000 67000 00000 00000 00000 20000 68000 68000 68000 20000 00000 00000	-3.785371000 -3.081738000 -1.690871000 -0.977623000 -1.690871000 0.392774000 1.639044000 3.01172000 -3.618473000 -1.140165000 -1.140165000 -3.618473000 4.206078000 5.372043000
12 (CH3) 5 7 6 8 6 1 1 1 6 6 1 1 1 1	2BNCO 0.9337960 -0.4826180 -1.6690560 -2.8377510 1.8941100 2.8667860 1.4614690 2.0967250 1.4649200 0.7497240 1.6877020 2.4091020	00 - 00 - 00 - 00 - 00 - 00 - 00 - 00 -	-0.0012 -0.2365 -0.0928 -0.0091 -1.2427 -1.0278 -2.1285 -1.5132 1.4782 2.2092 1.7639 1.5761	32000 79000 83000 15000 34000 82000 99000 22000 02000 68000 31000 29000	0.002291000 0.009688000 0.001014000 -0.004929000 0.457904000 0.477775000 -1.040652000 -0.010177000 -0.394258000 1.028711000 -0.554585000
16 C6H5B C C C C C C B C C H H H H	<pre>(CO) 2 -0.336302 -1.530464 -1.560976 -0.404317 0.787324 0.823987 -0.442326 0.611146 1.457113 -2.438856 -2.495424 1.696351 1.758256</pre>	0.0918 -0.1807 -0.2372 -0.0022 0.2811 0.3176 -0.0548 -0.6302 -1.0865 -0.3595 -0.4768 0.4855 0.5322	887 776 240 231 85 578 827 265 579 517 828 597 5226	-2.607730 -1.942545 -0.550740 0.211159 -0.476770 -1.869094 1.786444 2.622315 3.254471 -2.507562 -0.053616 0.079658 -2.376519	

Н	-0.310166	0.128054	-3.690958
С	-1.535768	0.465302	2.607093
0	-2.411939	0.879820	3.226772

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