Electronic Supplementary Information for Dalton Transactions

Dative σ- and π-bonding in boron-nitrogen compounds: molecular structures of $(CH_3)_2NB(CH_3)N(CH_3)B(CH_3)_2$ and $(CH_3)_2NN(B(CH_3)_2)_2$ determined by gas electron diffraction and quantum chemical calculations

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Table S1 Cartesian coordinates (in Å) for the open form of $Me_2NBMeNMeBMe_2$, Me = CH_3, (**1-o)** obtained by structure optimization at the MP2/6-311++G** level.

N1	-1.396002	-0.084594	-0.873801
B2	-0.805981	-0.371322	0.372822
N3	0.435727	0.323864	0.780188
B4	1.680036	0.204912	0.111525
C5	-2.538430	-0.811636	-1.403503
C6	-0.935934	0.945764	-1.790621
C7	-1.468927	-1.417868	1.371607
C8	0.381691	0.946117	2.112464
C9	1.831117	-0.620378	-1.235398
C10	2.978259	0.880918	0.737275
H11	-2.853171	-1.593256	-0.714201
H12	-3.382987	-0.132252	-1.575477
H13	-2.282200	-1.278315	-2.363396
H14	-0.178555	1.563231	-1.309953
H15	-0.509074	0.507074	-2.701245
H16	-1.781440	1.580638	-2.083329
H17	-0.976607	-1.416415	2.347247
H18	-2.538762	-1.249090	1.535095
H19	-1.367062	-2.434168	0.969566
H20	-0.653162	1.162902	2.391448
H21	0.813462	0.303005	2.888227
H22	0.928512	1.891727	2.109997
H23	0.931928	-1.137233	-1.578735
H24	2.180024	0.036876	-2.043020
H25	2.624990	-1.366657	-1.102191
H26	2.878408	1.973454	0.778843
H27	3.149026	0.552169	1.770092
H28	3.881670	0.655960	0.163644

Table S2 Cartesian coordinates (in Å) for the closed form of $Me_2NBMeNMeBMe_2$, Me = CH_3, (**1-c)** obtained by structure optimization at the MP2/6-311++G** level.

N1	-0.745223	-0.000000	-0.673298
B2	-0.758442	0.000000	0.887835
N3	0.600216	0.000000	1.075122
B4	0.930848	-0.000000	-0.455574
C5	-1.339554	-1.202551	-1.281500
C6	-1.339554	1.202551	-1.281500
C7	-2.045471	0.000000	1.788810
C8	1.469951	0.000000	2.224610
C9	1.633410	1.346707	-0.993204
C10	1.633410	-1.346707	-0.993204
H11	-0.956757	-2.094100	-0.785012
H12	-2.430478	-1.174587	-1.180190
H13	-1.080370	-1.250348	-2.343794
H14	-0.956757	2.094100	-0.785012
H15	-2.430478	.174587	-1.180190
H16	-1.080370	1.250348	-2.343794
H17	-1.797971	0.000000	2.854267
H18	-2.669498	0.880034	1.592331
H19	-2.669498	-0.880034	1.592331
H20	0.892591	0.000000	3.154377
H21	2.115276	-0.885607	2.217086
H22	2.115276	0.885607	2.217086
H23	1.236298	2.268666	-0.551621
H24	2.702899	1.315647	-0.746537
H25	1.575259	1.443673	-2.085659
H26	1.236298	-2.268666	0.551621
H27	2.702899	-1.315647	-0.746537
H28	1.575259	-1.443673	-2.085659

Table S3 Cartesian coordinates (in Å) for the closed form of $(Me_2B)_2NNMe_2$, Me = CH_3, (**2-c)** obtained by structure optimization at the MP2/6-311++G** level.

N1	-0.040658	0.000000	-0.385175
N2	-0.034949	-0.000000	1.066136
B3	1.358084	0.000000	0.173038
B4	-1.108916	-0.000000	-1.284434
C5	-0.547305	1.220827	1.700560
C6	-0.547305	-1.220827	1.700560
C7	2.202253	-1.356721	0.182840
C8	2.202253	1.356721	0.182840
C9	-0.726362	0.000000	-2.822886
C10	-2.635255	-0.000000	-0.844228
H11	-0.184769	2.083242	1.147542
H12	-1.641022	1.216723	1.701765
H13	-0.177618	1.257911	2.729246
H14	-0.184769	-2.083242	1.147542
H15	-1.641022	-1.216723	1.701765
H16	-0.177618	-1.257911	2.729246
H17	1.612370	-2.271921	0.078707
H18	2.897084	-1.335455	-0.666179
H19	2.822332	-1.446507	1.083907
H20	1.612370	2.271921	0.078707
H21	2.897084	1.335455	-0.666179
H22	2.822332	1.446507	1.083907
H23	0.353273	0.000000	-2.996694
H24	-1.153782	-0.876916	-3.324756
H25	-1.153782	0.876916	-3.324756
H26	-2.826717	-0.000000	0.231109
H27	-3.141006	0.874803	-1.271378
H28	-3.141006	-0.874803	-1.271378

Table S4 Cartesian coordinates (in Å) for the open form of $(Me_2B)_2NNMe_2$, Me = CH_3, (**2-o)** obtained by structure optimization at the MP2/6-311++G** level.

N1	-0.070528	0.010638	-0.062625
N2	-0.269591	0.066180	1.362607
B3	1.260520	-0.029396	-0.629114
B4	-1.339177	0.041486	-0.778607
C5	-0.131066	-1.230951	1.998469
C6	0.409763	1.169152	2.018122
C7	2.575718	-0.265119	0.224118
C8	1.523416	0.228780	-2.171919
C9	-1.487929	-0.369284	-2.298169
C10	-2.653384	0.418033	0.011367
H11	-0.825992	-1.930116	1.524559
H12	0.878587	-1.664461	1.951097
H13	-0.415711	-1.125528	3.049978
H14	0.179485	2.087327	1.471003
H15	-0.001932	1.262607	3.028189
H16	1.501313	1.073236	2.098589
H17	2.470679	-0.647244	1.237173
H18	3.225504	-0.949450	-0.335721
H19	3.130326	0.681736	0.276941
H20	0.775080	0.833200	-2.684467
H21	2.498424	0.715687	-2.287732
H22	1.600759	-0.727027	-2.706418
H23	-0.685483	-0.974530	-2.717819
H24	-2.431720	-0.915768	-2.410912
H25	-1.593704	0.530757	-2.918826
H26	-2.502207	1.233859	0.722536
H27	-3.480760	0.661020	-0.663051
H28	-2.967633	-0.447146	0.611683

Table S5 Experimental and calculated vibrational amplitudes, *l,* for $Me_2NBMeNMeBMe_2$ (**1-o**), obtained by GED and B3PW91/6-311++G** respectively. Amplitudes in pm (estimated standard deviations in parentheses in units of the last digit)

Bond distances	*l(exp)*	*l(calc)*
N1-B2	4.25(3)[a]	4.64
N3-B2	4.65(3)[a]	5.04
N3-B4	4.34(3)[a]	4.73
N1-C5	4.47(3)[a]	4.86
N1-C6	4.46(3)[a]	4.86
B2-C7	5.05(3)[a]	5.45
N3-C8	4.57(3)[a]	4.97
B4-C9	5.03(3)[a]	5.42
B4-C10	5.07(3)[a]	5.46
<C-H>	7.53(1)	7.81
Nonbonded distances		
N1···N3	7.32(6)[b]	6.25
B2···B4	8.27(6)[b]	7.20
N1···B4	12.04(6)[c]	10.87
N1···C7	7.84(6)[b]	6.77
N1···C8	[11.02]	11.02
N1···C9	[16.17]	16.17
N1···C10	[11.94]	11.94
B2···C5	7.51(6)[b]	6.44
B2···C6	7.57(6)[b]	6.50
B2···C8	8.65(6)[b]	7.58
B2···C9	12.86(6)[c]	11.69
B2···C10	7.34 (6)[d]	7.73
N3···C5	11.03(6)[c]	9.86
N3···C6	6.48(6)[d]	6.87
N3···C7	8.18(6)[b]	7.11
N3···C9	8.04(6)[b]	6.97
N3···C10	8.04(6)[b]	6.97
B4···C5	[15.60]	15.60
B4···C6	[12.65]	12.65
B4···C7	13.73(6)[c]	12.56
B4···C8	7.87(6)[b]	6.80
C5···C6	7.92(6)[b]	6.84
C5···C7	6.88 (6)[d]	7.27
C5···C8	[17.30]	17.30
C5···C9	[22.24]	22.24
C5···C10	[21.05]	21.05
C6···C7	11.74(6)[c]	10.57

C6···C8	[11.82]	11.82
C6···C9	[21.62]	21.62
C6···C10	[12.48]	12.48
C7···C8	15.63(6)[c]	14.46
C7···C9	[20.67]	20.67
C7···C10	[14.93]	14.93
C8···C9	7.00(6)[d]	7.39
C8···C10	13.00(6)[c]	11.83
C9···C10	8.97(6)[b]	7.90

[a, b, c, d] These *l*-values were refined with a constant difference.
Fixed *l*-values in square brackets [ ].

Table S6 Experimental and calculated vibrational amplitudes, *l,* for $(Me_2B)_2NNMe_2$ (**2-c)** , obtained by GED and B3PW91/6-311++G**, respectively. Amplitudes in pm (estimated standard deviations in parentheses in units of the last digit)

Bond distances	*l(exp)*	*l(calc)*
N1-N2	4.78(4)[a]	5.17
N1-B3	4.84(4)[a]	5.23
N1-B4	4.21(4)[a]	4.61
N2-B3	7.34(4)[a]	7.74
N2-C5	4.61(4)[a]	5.01
B3-C7	5.17(4)[a]	5.57
B4-C9	5.06(4)[a]	5.46
B4-C10	5.08(4)[a]	5.47
<C-H>	7.58(1)	7.79
Nonbonded distances		
N1···C5	7.39(6)[b]	7.41
N1···C7	7.91(6)[b]	7.92
N1···C9	7.48(6)[b]	7.50
N1···C10	7.02(6)[b]	7.04
N2···B4	6.66(6)[b]	6.68
N2···C7	8.91(6)[b]	8.92
N2···C9	[7.67]	7.67
N2···C10	11.62(7)[c]	11.77
B3···B4	6.82(6)[b]	6.83
B3···C5	9.35(6)[b]	9.36
B3···C9	13.15(7)[c]	13.29
B3···C10	[8.26]	8.26
B4···C5	15.09(7)[c]	15.23
B4···C7	[16.20]	16.20
C5···C6	7.12(6)[b]	7.14
C5···C7	[10.32]	10.32
C5···C8	13.80(7)[c]	13.94
C5···C9	[15.42]	15.42
C5···C10	27.28(7)[c]	27.42
C7···C8	8.31(6)[b]	8.33
C7···C9	[23.07]	23.07
C7···C10	[21.88]	21.88
C9···C10	8.24(6)[b]	8.26

[a, b, c,] These *l*-values were refined with a constant difference.
Fixed *l*-values in square brackets.

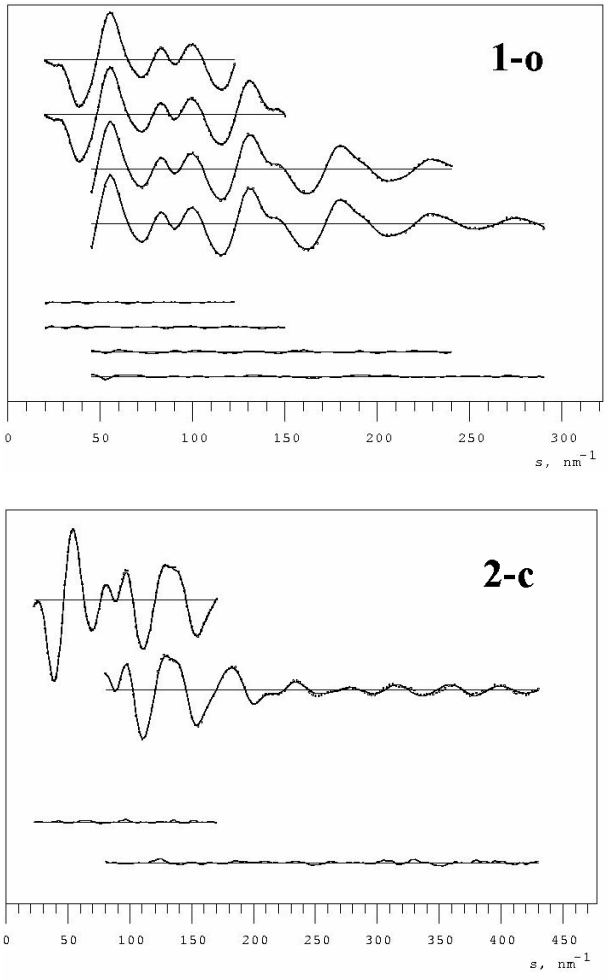

Figure S1 Experimental (dots) and calculated (lines) intensity curves of $Me_2NBMeNMeBMe_2$ (**1-o**) and $Me_2NN(BMe_2)_2$ (**2-c**).