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A Theoretical Investigation of Hydride Bridging in Chiral Oxazaborolidine-Borane Adducts: The Importance of Electron Correlation

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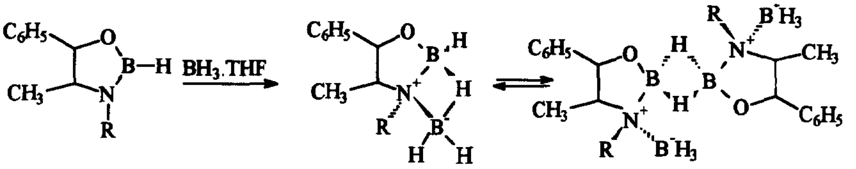
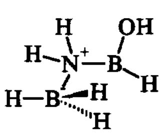
Abstract: Molecular-orbital calculations performed using the *ab initio* MP2/6-31G** and semi-empirical AM1 methods predict hydride bridging to be favoured in oxazaborolidine-borane adducts, in agreement with experiment but in contrast to the *ab initio* HF/6-31G** method. These results indicate the importance of electron correlation effects for a correct theoretical description of the structure and energies of these bridged species of importance for mechanistic studies of asymmetric induction by chiral oxazaborolidine-borane adducts.

Introduction:

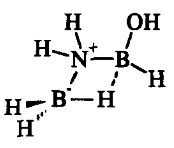
Chiral oxazaborolidine-borane adducts have been shown to be highly effective for the enantioselective reduction of prochiral ketones.1 The efficiency of the catalytic behaviour of these species is dependent on the stability of the oxazaborolidine-borane adduct. Recent work has revealed that the adduct can undergo dimerisation[2] to form a more stable bridged species. The ^{11}B and ^{13}C NMR study by Tlahuext and Contreras[2a] revealed that dimerisation was preceded by the formation of a hydride-bridged monomer.



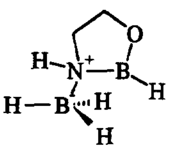
To investigate the stability of the bridged monomer species we have undertaken an *ab initio* and semi-empirical molecular orbital study of two model systems, one acyclic and one cyclic.



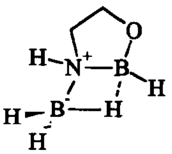
1a



1b



2a



2b

Computational methods:

Ab initio MO calculations were performed using GAUSSIAN 92,[3] with the 6-31G** basis at the level of both Hartree-Fock self-consistent field theory (HF) and second-order Møller-Plesset perturbation theory (MP2). Semi-empirical calculations were performed using MOPAC 93[4] with the AM1 hamiltonian. Each species was subjected to full geometry optimisation and was characterised as corresponding to either an energy minimum or a saddle point on the energy hypersurface by determination of the Hessian matrix of second derivatives of the energy with respect to nuclear displacements: a transition structure possesses a single imaginary vibrational frequency whereas a minimum-energy structure has none.

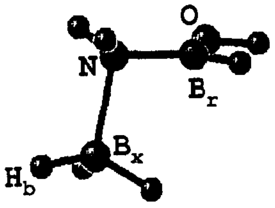
Results and Discussion:

Energies and geometries for optimised structures are given in Tables 1, 2 and 3.

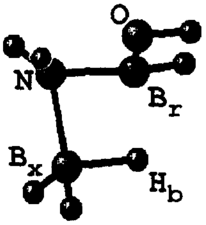
Table 1: Total energies (hartree)^a for *ab initio* and heats of formation (kJ mol^{-1}) for semi-empirical MO optimised structures

Structure	MP2/6-31G**	HF/6-31G**	AM1
1a	-183.38957	-182.83666	-453.71
1b	-183.39739	-182.83384	-490.03
2a	-260.54487	-259.72311	-327.70
2b	-260.55138	-259.71997	-370.24

^{a} Total energy in hartrees (1 hartree = 2625 kJ mol^{-1})



1a

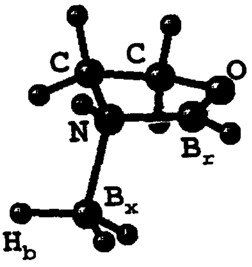


1b

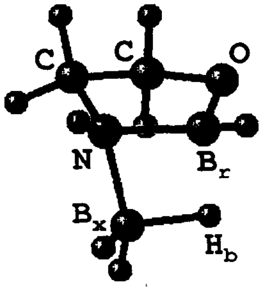
Table 2: Bond lengths (Å), angles (°) and the number of imaginary frequencies (NIMAG) for optimised structures **1a** and **1b**

	MP2/6-31G**		HF/6-31G**		AM1	
	1a	**1b**	**1a**	**1b**	**1a**	**1b**
N-B_r	1.476	1.583	1.468	1.522	1.454	1.527
N-B_x	1.707	1.538	1.750	1.604	1.582	1.534
B_r-$H_{nearest}$	2.466	1.427	2.683	1.527	2.395	1.386
B_x-$H_{bridged}$	-	1.286	-	1.280	-	1.327
B_x-$H_{non\text{-}bridged}$	1.202	1.189	1.206	1.194	1.209	1.200
N-B_x-$H_{bridged}$	-	96.9	-	97.0	-	95.9
N-B_x-$H_{non\text{-}bridged}$	104.4	112.5	103.5	111.7	105.7	115.5
B_x-H_b-B_r	-	92.2	-	91.7	-	91.4
B_r-N-B_x	101.3	77.6	106.0	80.5	97.1	78.8
B_r-N-B_x-H_b	157.5	1.8	-168.3	0.8	171.3	-2.2
NIMAG	1^a	0	0	0	1^b	0

^{a} $\nu^{\ddagger} = 101i$ cm^{-1} ^{b} $\nu^{\ddagger} = 127i$ cm^{-1}



2a



2b

Table 3: Bond lengths (Å), angles (°) and the number of imaginary frequencies (NIMAG) for optimised structures **2a** and **2b**

	MP2/6-31G**		HF/6-31G**		AM1	
	2a	**2b**	**2a**	**2b**	**2a**	**2b**
$N\text{-}B_r$	1.493	1.558	1.485	1.543	1.493	1.567
$N\text{-}B_x$	1.684	1.574	1.719	1.587	1.599	1.544
$B_r\text{-}H_{nearest}$	2.595	1.414	2.672	1.479	2.284	1.360
$B_x\text{-}H_{bridged}$	-	1.298	-	1.296	-	1.338
$B_x\text{-}H_{non\text{-}bridged}$	1.204	1.190	1.207	1.194	1.209	1.200
$N\text{-}B_x\text{-}H_{bridged}$	-	97.2	-	97.0	-	96.2
$N\text{-}B_x\text{-}H_{non\text{-}bridged}$	104.6	112.9	104.4	112.5	105.5	112.8
$B_x\text{-}H_b\text{-}B_r$	-	92.2	-	91.9	-	91.9
$B_r\text{-}N\text{-}B_x$	102.8	77.3	105.4	79.4	100.3	77.2
$B_r\text{-}N\text{-}B_x\text{-}H_b$	[a]	-2.3	-169.8	-2.7	148.4	-5.1
NIMAG	-	0	0	0	1[b]	0

[a] Dihedral angle constrained at 180°

[b] $\nu^{\ddagger} = 150i$ cm^{-1}

The bridged structures **1b** and **2b** are predicted to be energy minima at each level of theory. The HF/6-31G** method also predicts the non-bridged structures **1a** and **2a** to be minima, about 7 or 8 kJ mol^{-1} lower in energy that the bridged structures; this results accords with Nevalainen's conclusion[5] from small-basis *ab initio* HF calculations, that bridging is not favourable. However, the MP2/6-31G** method (which includes the most important effects of electron correlation) and the AM1 method (which implicitly includes electron-correlation effects by virtue of its parameterisation) both predict the non-bridged structures to be first-order saddle points for internal rotation about the $N\text{-}B_x$ bond. The bridged structures are about 20 kJ mol^{-1} lower in energy than the non-bridged one at the MP2/6-31G** levels and about 40 kJ mol^{-1} at the AM1 level, (Table 4).

Table 4: Bridging energies (kJ mol^{-1})

	MP2/6-31G**	HF/6-31G**	AM1
E(**1b**) - E(**1a**)	-20.5	7.4	-36.3
E(**2b**) - E(**2a**)	-18.1	8.2	-42.5

A structural measure of the degree of bridging is provided by the Pauling bond order n calculated as $n = \exp[(d_1 - d_n)/c]$ where d_1 and d_n are the bond lengths of order 1 and n respectively and c is a constant whose value is determined by assuming the bridging B-H bonds in diborane to have $n = 0.5$. Values for c of 0.177, 0.190 and 0.198 were obtained for the MP2, HF and AM1 methods respectively. The calculated bond orders (Table 5) are consistent in showing a greater degree of bonding of the bridging H to B_x than to B_r, with the asymmetry being greatest for HF/6-31G** and least for AM1, in accord with the bridging energies. No asymmetric structure with a short, stronger bond between the bridging H and B_r and could be located as a stationary point on the energy hypersurface: presumably the contribution from B-O: ↔ $^-B=O^+$ resonance favours **1b** and **2b** rather than the alternatives with bridging H closer to B_r.

Table 5: Pauling bond orders for bridged structures

	MP2/6-31G**		HF/6-31G**		AM1	
	1b	**2b**	**1b**	**2b**	**1b**	**2b**
B_x-$H_{bridged}$	0.56	0.52	0.61	0.56	0.51	0.48
B_r-$H_{bridged}$	0.25	0.27	0.17	0.21	0.38	0.43

Conclusion:

This study shows the importance of electron correlation effects upon the structures and energies of borane adducts. The formation of bridged species was found to be energetically favoured for chiral oxazaborolidine-borane adducts using either the *ab initio* MP2/6-31G** or the semi-empirical AM1 method, in accord with experiment. Theoretical results obtained for the adducts using *ab initio* HF methods without electron correlation should be regarded with caution. In contrast AM1 correctly describes these bridging interactions and provides a suitable method for theoretical study of the mechanism of asymmetric induction by these interesting catalysts.

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