Inorg. Chem. **1988**, *27*, 3987–3992 **3987**

results of this study have relevance far beyond the specific class of fluorinated amines treated here theoretically, however, and the conceptual connections of this work with a broad range of main-group chemical species in which negative hyperconjugation can play an important role in stabilizing ground or transition structures was hinted at in our discussion in section IV. Furthermore, our earlier conclusions[2a,66] concerning the general phenomenon of negative hyperconjugation have been reconfirmed and extended.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, the Bundesministerium für Forschung und Technik, and Convex Computer Corp. A study of $FSiH_2NH_2$ was suggested by Prof. Epiotis, whom we thank for his stimulation.

Registry No. $HBeNH_2$, 50688-89-6; $FBeNH_2$, 116377-34-5; H_2BNH_2, 14720-35-5; $FBHNH_2$, 116377-35-6; F_2BNH_2, 50673-31-9; H_3CNH_2, 74-89-5; FCH_2NH_2, 36336-09-1; F_2CHNH_2, 47950-15-2; F_3CNH_2, 61165-75-1; H_2NNH_2, 302-01-2; $FNHNH_2$, 36336-10-4; F_2NNH_2, 115967-51-6; $HONH_2$, 7803-49-8; $FONH_2$, 36405-65-9; $HMgNH_2$, 116377-36-7; $FMgNH_2$, 116377-37-8; H_2AlNH_2, 53138-60-6; $FAlHNH_2$, 116377-38-9; F_2AlNH_2, 116377-39-0; H_3SiNH_2, 13598-78-2; $FSiH_2NH_2$, 116377-40-3; F_2SiHNH_2, 116377-41-4; F_3SiNH_2, 116377-42-5; H_2PNH_2, 13598-67-9; $FPHNH_2$, 14616-21-8; F_2PNH_2, 25757-74-8; $HSNH_2$, 14097-00-8; $FSNH_2$, 36579-30-3; $ClSNH_2$, 13812-03-8.

Supplementary Material Available: GAUSSIAN 82 archive entries (same format as in ref 32a) of the HF/6-31G* and MP2FU/6-31G* geometry optimizations, HF/6-31G* frequency, and MP2FC/6-31G* and MP4SDTQ/6-31+G* energy calculations performed in this work, the complete geometries being specified (22 pages). Ordering information is given on any current masthead page.

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Dilithiodiborane(6) ($Li_2B_2H_4$): An Experimentally Viable Species with a B=B Double Bond. Planar No-Bond–Double-Bond Isomers with Pentacoordinate Boron?†

Elmar Kaufmann* and Paul von Ragué Schleyer

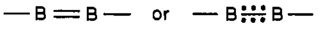
Received March 14, 1988

The title compound **6a**, the all-planar dilithium derivative of the tetrahydrodiborate(2−) dianion, $B_2H_4^{2-}$, is calculated to be a highly stable species thermodynamically with a B=B double bond of length 1.613 Å (6-31G* data). All possible decomposition reactions are endothermic, and the dissociation energy ($Li_2B_2H_4 \rightarrow 2LiBH_2$) is 117.9 kcal/mol (MP2/6-31G*//6-31G* + ZPE). Other isomers of dilithiodiborane(6), $Li_2B_2H_4$, which correspond to minima, are derivatives of diborane(6), B_2H_6, with both lithiums in terminal (**5**) or in bridging (**4a**) positions. Their relative energies are 77.9 and 82.9 kcal/mol, respectively (MP2/6-31G*//6-31G* + ZPE). Attractive ("agostic") Li–H interactions are responsible for the planar conformations of **6a** and **4a**. The barrier for converting **4a** into **6a** ("no-bond–double-bond isomerism", a form of bond-stretch isomerism) is too small (only 4.9 kcal/mol at MP2/6-31G*//6-31G* + ZPE) to be able to predict the existence of **4a**.

Introduction

Since the basic work of Stock[1] the number of known boron hydrides and hydroborate anions has been growing extensively, including compounds containing up to 30 boron atoms.[2] Most of them are characterized by delocalized multicenter bonds because of their electron-deficient nature. However, despite the variety of their structures, none of them have been found to exhibit a boron–boron double bond.

The simplest molecule expected to have such a boron–boron π-bond is diborane(2), B_2H_2. Theoretical studies[3-5] indicate its ground state to be a triplet[5] with the two degenerate π orbitals singly occupied. Experimentally, only nonstoichiometric polymeric $(BH_x)_n$ compounds are known with x close to 1.[6] The polymerization energy of B_2H_2 has been calculated to be about 260 kcal/mol.[4] Formal halogen derivatives of B_2H_2 are "oligomeric" and have cluster structures, e.g., B_nCl_n (n = 4, 8, 9).[7] However, the ion $B_2Cl_2^+$ has been observed in the mass spectral fragmentation of B_2Cl_4,[8a] and the doubly charged ion B_2^{2+} has been produced in a metastable state in a tandem accelerator.[9] Koch et al.[10] examined the helium-substituted derivative B_2He_2 calculationally but did not find it to be a minimum. A less "exotic" approach to a B=B π-bond was suggested quite recently theoretically by Jouany, Barthelat, and Daudey:[5] Substitution of H in B_2H_2 by amino groups should lead to the singlet-ground-state molecule $H_2NB{=}BNH_2$, isoelectronic with butatriene, $H_2C{=}C{=}C{=}CH_2$. However, no boron–boron double bond with dicoordinated boron has been characterized experimentally. The reason seems to be the extreme electrophilic nature of structures of type **1** (which also may be represented as having two partial π-bonds).



1

Compounds involving boron and exhibiting double-bond character are known with, e.g., nitrogen and phosphorus.[11] There

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† Dedicated to Prof. H. Nöth on the occasion of his 60th birthday.

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Table I. Total (au) and Zero-Point Vibrational Energies (kcal/mol) of Neutral Species

species	structure or state	no.	point group	3-21G// 3-21G	6-31G*// 6-31G*	MP2/ 6-31G*// 6-31G*	ZPE[a]
H_2			$D_{\infty h}$	−1.122 96[b]	−1.126 83[b]	−1.144 10[b]	6.66 (0)
LiH			$C_{\infty v}$	−7.929 84[b]	−7.980 87[b]	−7.995 96	2.04 (0)
Li_2			$D_{\infty h}$	−14.769 25[b]	−14.866 92[b]	−14.885 43	0.49 (0)
BH_3			D_{3h}	−26.237 30[b]	−26.390 01[b]	−26.464 23[b]	17.29 (0)
$LiBH_2$	$^1A_1$		C_{2v}	−33.013 85[b]	−33.209 94[b]	−33.291 90	11.62 (0)
Li_2BH	$^1A_1$		C_{2v}	−39.789 32	−40.028 23	−40.124 29	6.50 (0)
B_2H_2	$^1\Delta_g$		$D_{\infty h}$	−50.102 20[b]	−50.384 11[b]	−50.508 38	14.65 (0)
B_2H_4			D_{2d}	−51.339 74[b]	−51.634 71[b]	−51.777 14	25.69 (0)
B_2H_6			D_{2h}	−52.497 81[b]	−52.812 40[b]	−52.992 59[b]	41.77 (0)
LiB_2H_3	invert	**7d**	C_{2v}	−58.119 84	−58.451 66	−58.622 37	20.65 (1)
	perp	**7b**	C_s	−58.143 93	−58.477 47	−58.646 01	20.40 (0)
	planar	**7c**	C_{2v}	−58.128 23	−58.469 32	−58.656 12	20.87 (1)
	folded	**7a**	C_s	−58.132 23	−58.473 73	−58.658 26	20.31 (0)
$Li_2B_2H_2$	H-brid	**8c**	C_{2v}	−64.887 51	−65.282 69	−65.479 36	13.97 (0)
	planar	**8b**	D_{2h}	−64.970 29	−65.348 84	−65.550 19	13.34 (1)
	Li-brid	**8a**	C_{2v}	−64.971 35	−65.350 56	−65.551 84	16.30 (0)
$(LiBH_2)_2$	perp	**4b**	D_{2h}	−66.070 43	−66.458 75	−66.625 72	24.30 (2)
	planar	**4a**	D_{2h}	−66.086 49	−66.475 51	−66.641 48	24.56 (0)
	H-brid	**5**	C_{2h}	−66.047 17	−66.449 24	−66.655 00	28.42 (0)
$Li_2B_2H_4$	"TS"	**10a**	C_{2h}	−66.049 53	−66.441 34	−66.621 15	23.80 (2)
	"TS"	**10b**	C_s	−66.063 90	−66.453 40	−66.632 56	24.59 (2)
	TS[c]	**11**	C_1	−66.064 81	−66.454 59	−66.634 49	25.15 (1)
$Li_2B_2H_4$	invert	**6c**	D_{2h}	−66.115 81	−66.504 39	−66.711 08	27.73 (2)
	perp	**6b**	D_{2h}	−66.158 09	−66.546 48	−66.753 05	26.77 (2)
	planar	**6a**	D_{2h}	−66.182 17	−66.573 09	−66.780 62	29.46 (0)

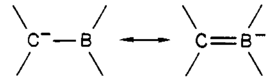
[a] Zero-point energy at 3-21G; number of imaginary frequencies in parentheses. [b] Reference 27. [c] Transition structure for the interconversion of **4a** and **6a**.

Table II. Total (au) and Zero-Point Vibrational Energies (kcal/mol) of Anionic Species

species	structure or state	no.	point group	3-21G// 3-21G	6-31+G*// 6-31+G*	MP2/ 6-31+G*// 6-31+G*	ZPE[a]
$B_2H_3^-$	linear	**9b**	C_{2v}	−50.706 20[b]	−51.012 97	−51.178 09	18.58 (0)
	brid	**9a**	C_{2v}	−50.695 44[b]	−51.006 06	−51.187 17	18.34 (0)
$B_2H_4^{2-}$		**3**	D_{2h}	−51.057 22	−51.441 66	−51.631 10	22.93 (0)
$B_2H_4^{\bullet-}$	$^2B_{3u}$		D_{2h}	−51.332 03	−51.637 71	−51.799 11	24.80 (0)

[a] Zero-point energy at 3-21G; number of imaginary frequencies in parentheses. [b] Reference 27.

are also numerous examples of α-metalated alkylboranes; the corresponding ion, **2**, is isoelectronic with ethylene. Anions of this

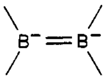


2

type have been extensively used for synthetic purposes.[12] There is spectroscopic[13] and calculational[14] evidence for substantial π-bond character in these compounds.

The first *neutral* compound with a boron–carbon double bond involving dicoordinated boron was described in 1983[15a] and examined theoretically.[16] Other examples have been found more recently[15b] and X-ray structural analyses reported.[17] In this context it should be mentioned that diboriranides, which also formally are α-metalated boranes, appear to have considerable B–B double-bond character.[18]

Reduction of diborane(4) derivatives results in the formation of radical anions, $R_2B{-}BR_2^{\bullet-}$. These one-electron π-bond species have been characterized by ESR.[19] Further reduction should lead to the dianion **3**, which is the isoelectronic dibora analogue of



3

ethylene. This dianion is unknown, although a formal derivative, incorporated in a benzene ring (a 1,2-diboratabenzene), has been prepared very recently.[20] We now describe species based on dianion **3**, which we discovered during our general investigation of the aggregation of lithium compounds.[21]

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Table III. Relative Energies (kcal/mol) of LiB_2H_3, $Li_2B_2H_2$, and $Li_2B_2H_4$ Isomers at Various Levels

species	structure	no.	point group	3-21G//3-21G	6-31G*//6-31G*	MP2/6-31G*//6-31G*	Δ(ZPE)[a]	final est[b]
LiB_2H_3	invert	**7d**	C_{2v}	15.1	16.2	22.5	+0.3	22.8
	perp	**7b**	C_s	0.0	0.0	7.7	+0.1	7.8
	planar	**7c**	C_{2v}	9.9	5.1	1.3	+0.5	1.8
	folded	**7a**	C_s	7.3	2.3	0.0	0.0	0.0
$Li_2B_2H_2$	H-brid	**8c**	C_{2v}	52.6	42.6	45.5	-2.1	43.4
	planar	**8b**	D_{2h}	0.7	1.1	1.0	0.0	1.0
	Li-brid	**8a**	C_{2v}	0.0	0.0	0.0	0.0	0.0
$(LiBH_2)_2$	perp	**4b**	D_{2h}	70.1	71.7	97.2	-4.6	92.6
	planar	**4a**	D_{2h}	60.0	61.2	87.3	-4.4	82.9
	H-brid	**5**	C_{2h}	84.7	77.7	78.8	-0.9	77.9
$Li_2B_2H_4$	"TS"	**10a**	C_{2h}	83.2	82.7	100.1	-5.1	95.0
	"TS"	**10b**	C_s	74.2	75.1	92.9	-4.4	88.5
	TS[c]	**11**	C_1	73.6	74.4	91.7	-3.9	87.8
$Li_2B_2H_4$	invert	**6c**	D_{2h}	41.6	43.1	43.6	-1.6	42.0
	perp	**6b**	D_{2h}	15.1	16.7	17.3	-2.4	14.9
	planar	**6a**	D_{2h}	0.0	0.0	0.0	0.0	0.0

[a] Difference in zero-point energies, scaled by 0.9.[26] [b] Final estimates evaluated by using data from the highest level employed plus Δ(ZPE). [c] Transition structure for the interconversion of **4a** and **6a**.

Table IV. Energies (kcal/mol)[a] of Dimerization and Decomposition Reactions

reacn	eq no.	3-21G//3-21G	6-31G*//6-31G*	MP2/6-31G*//6-31G*	Δ(ZPE)[b]	final est[c]
$2LiBH_2 \rightarrow$ **4a**	1	-36.9	-34.9	-36.2	+1.2	-35.0
$2BH_3 \rightarrow B_2H_6$	2	-14.6	-20.3	-40.2	+6.5	-33.7
$2LiBH_2 \rightarrow$ **5**	3	-12.2	-18.4	-44.7	+4.7	-40.0
$Li_2B_2H_4$ (**6a**) $\rightarrow$						
$2LiBH_2$	4	96.9	96.1	123.5	-5.6	117.9
$Li_2BH + BH_3$	5	97.6	97.2	120.5	-5.1	115.4
$LiB_2H_3 + LiH$	6	68.0	72.0	79.3	-6.4	72.9
$B_2H_4 + Li_2$	7	45.9	44.8	74.1	-3.0	71.1
$Li_2B_2H_2 + H_2$	8	55.1	60.1	53.1	-5.8	47.3
LiB_2H_3 (**7**) $\rightarrow$						
B_2H_2 ($^1\Delta_g$) + LiH	9a	70.2	70.6	96.6	-3.3	93.3
B_2H_2 $^3\Sigma_g^-$) + LiH	9b					76.7[d]

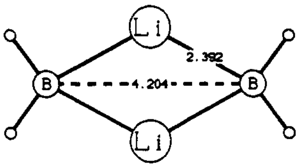
[a] All species in their most stable conformations at the levels indicated. [b] Difference in zero-point energies, scaled by 0.9.[26] [c] Final estimates evaluated using data from the highest level employed plus Δ(ZPE). [d] Calculated by using data from ref 5.

We also discuss $B_2H_3^-$ anions and their metal derivatives. These are isoelectronic with the vinyl cation and also possess B═B double bonds.

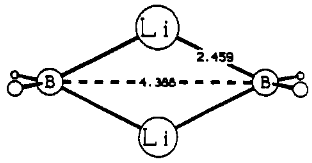
Calculational Methods

We followed standard procedures:[22] geometries were fully optimized within the designated symmetry constraints at the restricted (closed-shell species) or unrestricted (open-shell species) Hartree–Fock level using the 3-21G and 6-31G* basis sets[23] incorporated in the GAUSSIAN 76 and GAUSSIAN 82 program systems.[24] Only singlet states were considered for even-electron systems. Anions were calculated with the diffuse function-augmented basis set 6-31+G*,[23] which improves the description of negatively charged species. Electron correlation was estimated with the 6-31G* (6-31+G* for anions) basis sets by using Møller–Plesset theory

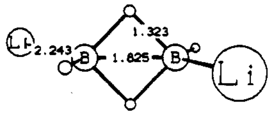
Chart I



4a, D_{2h}
82.9



4b, D_{2h}
92.6



5, C_{2h}
77.9

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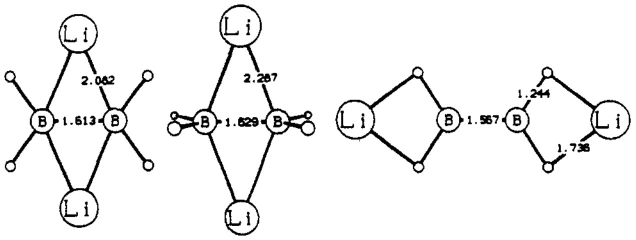
Chart II



6a, D_{2h} 0.0 **6b**, D_{2h} 14.9 **6c**, D_{2h} 42.0

carried out to second order (MP2)[25] and keeping the core electrons frozen. Frequency analyses were carried out with the 3-21G basis set. Final energy estimates were obtained by adding the differences in zero-point energies (ZPE), scaled by the empirical factor 0.9,[26] to the MP2/6-31G*//6-31G* data. Only these final estimates will be discussed. Total energies and ZPEs are listed in Tables I and II and relative and reaction energies in Tables III and IV. Relative isomer energies (in kcal/mol) together with important bond lengths (in Å, at 6-31G*) are also given in the charts. Some reference energies were taken from ref 27. Charges and bond orders were obtained by natural population analysis (NPA).[28] Full geometry information in the form of archive entries[27] is available as supplementary material. Molecular orbital plots were performed with a modified version of Jorgensen's program PSI/77.[29]

Results and Discussion

Lithioborane(3), $LiBH_2$ singlet ($^1A_1$), forms two highly symmetric dimers (lower symmetry alternatives are less stable): the all-planar **4a** (D_{2h}), which has the usual four-center quadrupole structure of LiX dimers,[21] and the doubly hydrogen bridged isomer **5** (C_{2h}), which can be regarded as a terminally dilithiated derivative of diborane(6).

The dimerization energy of **4a** with two bridging lithiums is −35.0 kcal/mol (eq 1). At the same level of theory (MP2/6-31G*//6-31G* + ZPE) the energy gained on formation of diborane(6) with two bridging hydrogens is almost the same, −33.7 kcal/mol (eq 2). This value is close to the best available ab initio data (−37.0 ± 3[30a] and −33.9 kcal/mol[30b] at 0 K), indicating that our level of theory is quite adequate. When terminal lithiums are present (**5**), the dimerization energy is increased to −40.0 kcal/mol (eq 3).

$$2LiBH_2 \rightarrow \mathbf{4a} \quad -35.0\ \text{kcal/mol} \tag{1}$$

$$2BH_3 \rightarrow B_2H_6 \quad -33.7\ \text{kcal/mol} \tag{2}$$

$$2LiBH_2 \rightarrow \mathbf{5} \quad -40.0\ \text{kcal/mol} \tag{3}$$

Both **4a** and **5** are minima (no imaginary frequencies at 3-21G), whereas the perpendicular arrangement **4b** (despite its obvious structural relationship to diborane(6)) is a higher order stationary point (two imaginary frequencies corresponding to con- and disrotation of the BH_2 groups). The unusual planar tetracoordination of the boron atoms in **4a** is due to attractive Li–H interactions. The lithiums are highly ionic (NPA charges[28] +0.777), and the hydrogens have hydridic character (charge −0.150). The hydrogen-bridged **5**, which was not described in our previous study of LiX dimerization,[21a] is 5 kcal/mol more stable than the planar **4a**. The reversal of relative energies of **4** and **5** at the SCF and at correlated levels results from the importance of electron correlation for B_2H_6 and other hydrogen-bridged boron compounds.[30]

Shortening the B–B distances in **4** results in structures that are "dimers" of $LiBH_2$ only in a formal sense: **6a** and **6b** are not merely held together by Coulombic attractions of positively charged lithium ions and the negative BH_2 groups but also possess strong covalent boron–boron bonds *essentially double in nature.* Since lithium–hydrogen agostic interactions are often important in influencing the structures of lithium compounds,[21d,31] we also examined the doubly inverted structure **6c**. All these isomers (**6a–c**) are derivatives of the tetrahydrodiborate(2−) anion **3**. This dianion is not a viable species as an isolated entity since it is not bound with respect to loss of an electron: The π HOMO has an energy of +0.171 au, whereas the π SOMO of the corresponding radical anion, $B_2H_4^{\bullet -}$, has an energy of −0.047 au (6-31+G* data). The presence of two lithium counterions in the $Li_2B_2H_4$ isomers results in the stabilization of the negative charges due to attractive Coulombic interactions: the energies of the HOMOs (which are all π type) of **6a–c** are −0.208, −0.219, and −0.157 au, respectively (6-31G* data). Like **4a**, planar **6a** is a minimum and is more stable (by 14.9 kcal/mol) than the perpendicular structure **6b** (two imaginary frequencies). The doubly inverted structure **6c** also is a higher order stationary point (two imaginary frequencies). Its relative energy is 42.0 kcal/mol (Table III). Nevertheless, it is considerably more stable than any of the dimer structures **4** and **5**.

B–B Bond Lengths. The B–B bond lengths in **6a–c** are 1.613, 1.629, and 1.567 Å, respectively (6-31G* data). Despite the adjacent negative charges these lengths are at least 0.1 Å shorter than the experimentally determined boron–boron separations in tetrachlorodiborane(4) (1.75 ± 0.05 Å, X-ray;[32a] 1.70 ± 0.07 Å, electron diffraction[32b]), in tetrabromodiborane(4) (1.69 ± 0.02 Å, electron diffraction),[33] or in the tetrahedral cluster B_4Cl_4 (1.70 ± 0.04 Å).[7a] Even the B–B bond in B_2F_4, which is shortened due to the strong electron withdrawal by the fluorine substituents, is longer by 0.06–0.11 Å: the B–B separations in solid and gaseous B_2F_4 are 1.67 ± 0.05 (X-ray)[34a] and 1.72 Å (electron diffraction),[34b] respectively. B–B bond lengths of organic derivatives of diborane(4), B_2H_4, determined experimentally by X-ray structural analyses, are 1.698 (4)[35] and 1.711 (6) Å.[36] A zinc-complexed base adduct of B_2H_4 itself has a 1.814 (6) Å B–B bond.[37] Thus, the B–B separations in **6** are shorter than any known B–B single bond and are between those calculated for the neutral species $H_2B—BH_2$ (1.653–1.679 and 1.742–1.762 Å in perpendicular and planar conformations, respectively)[27,38] and

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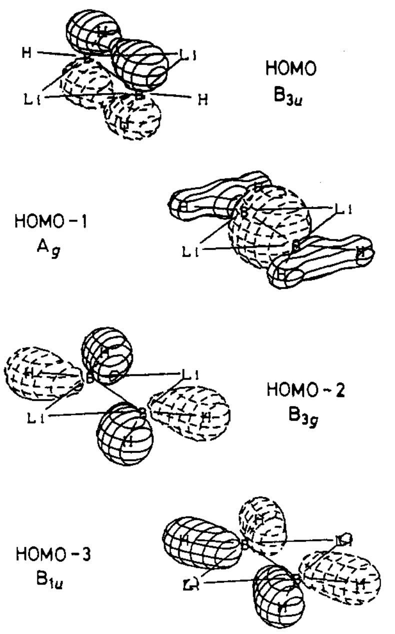


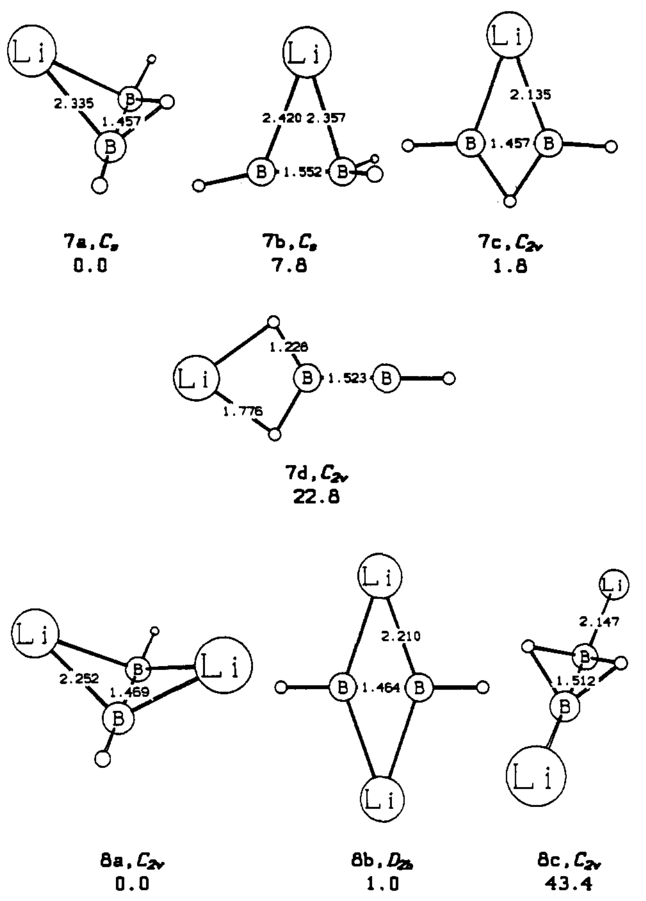
Figure 1. The four highest occupied molecular orbitals of B=B double-bonded **6a**.

$HB{=}BH$ (1.498–1.515 Å, depending on the electronic state).[5,27] B_2H_2 has the B=B distance (average 1.51 Å) expected by analogy with carbon systems: e.g., ethene, 1.317 Å, vs ethane, 1.528 Å (6-31G* data).[27] That is, the B=B bond length in B_2H_2 is about 0.2 Å shorter than the single bond in B_2H_4 (average 1.71 Å). The up to 0.12 Å longer B=B double bonds in **6a–c** result from the repulsion of the two adjacent negative charges. This electrostatic elongation effect also is clearly seen in the doubly bonded series B_2H_2, $B_2H_3^-$ (linear **9b**), and $B_2H_4^{2-}$, where the B=B bond lengths are 1.510 (6-31G*),[27] 1.557, and 1.673 Å (6-31+G*), respectively.

B–B Bond Energies. Combining two $LiBH_2$ units to form **6a** results in an energy gain of 117.9 kcal/mol (Table IV)! Part of this energy of course stems from the bridging by two lithium cations (e.g., the dimerization energy of $LiBH_2$ to give **4a** is –35.0 kcal/mol; eq 1), but the experimentally known energies of boron–boron single bonds determined thermochemically are only 79 (B_2Cl_4)[39a] and 72.4 kcal/mol (B_2F_4).[39b] However, in a mass spectrometric study of photoionization Dibeler et al.[8] derived B–B bond energies in B_2Cl_4 and B_2F_4 of 87.6 and 103 kcal/mol, respectively. Nevertheless, **6a** seems to be a highly stable species thermodynamically. By the approved nomenclature,[2b] this remarkable compound should be named "dilithiodiborane(6)" or "dilithium tetrahydrodiborate(2–).

Electronic Structure of Dilithiodiborane(6). The planar **6a** (and also the perpendicular **6b**) are essentially $B_2H_4^{2-}$ anions associated with two lithium cations. The charges on lithium are +0.928 and +0.863, respectively, according to natural population analysis (at 3-21G). The hydrogens are hydridic (charge –0.103 and –0.060, respectively). Figure 1 shows the four highest occupied molecular orbitals of **6a**. There is considerable mixing of the σ_{BH_2} group orbitals with the B–B σ-bond (HOMO-1, A_g). The HOMO (B_{3u}) is a pure B–B π-bond. The contribution of the diffuse lithium p orbitals is too small to be seen in the plot. The highly ionic character of **6a** prohibits cyclic π delocalization.[40] A small contribution of lithium orbitals can be seen in HOMO-3 (B_{1u}) corresponding to a weak antibonding interaction of lithium with the symmetric combination of the π_{BH_2} group orbitals. The stabilizing Li–H interactions mentioned above are mainly electrostatic in nature. Since **6a** is more stable than **6b** by 14.9 kcal/mol (Table III), the interaction is about 3.7 kcal/mol per Li–H contact. With substituents other than hydrogen (e.g., alkyl groups) conformations corresponding to **6b** may well become more stable.

Chart III



Thermodynamic Stability of Dilithiodiborane(6). In order to demonstrate the stability of **6a**, we calculated the energies of all reasonable decomposition reactions. Some of the decomposition products, which have not yet been described in the literature, are shown in Chart III. As mentioned above, the disruption into two $LiBH_2$ molecules is endothermic by 117.9 kcal/mol (Table IV, eq 4). Splitting off BH_3 also is very unfavorable (+115.4 kcal/mol, eq 5). Decomposition into lithium hydride and lithiodiborane(4) (**7a**), or into a lithium molecule and diborane(4), still requires 72.9 and 71.1 kcal/mol, respectively (eq 6 and 7). Considering the lattice energies of LiH and Li_2 (54.1 and 50.3 kcal/mol at 0 K),[41] these decomposition reactions are still endothermic by 18.8 and 20.8 kcal/mol, respectively. The most favorable reaction in this context is the elimination of H_2 to form 1,2-dilithiodiborane(4) (**8a**), which requires 47.3 kcal/mol (eq 8).

The product of decomposition reaction 6 (Table IV), lithiodiborane(4), is a derivative of the trihydrodiborate(1–) anion **9**. The bridged form **9a** is 5.9 kcal/mol more stable than the linear **9b** (calculated from the data in Table II). This is similar to the case for the isoelectronic vinyl cation, where the bridged form (corresponding to **9a**) also is the most stable structure.[42] Extensive

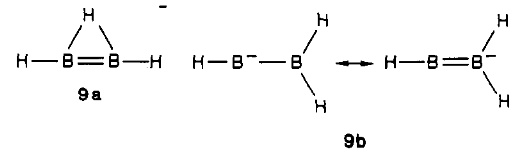


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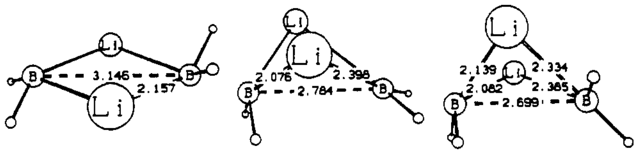
Chart IV



10a, C_{2h} 95.0 **10b**, C_s 88.5 **11**, C_1 87.8

delocalization of the negative charge in both **9a** and **9b** leads to B=B double bonds of lengths 1.465 and 1.557 Å (6-31+G*), respectively. Thus, the B–B separation in **9a** is even shorter than that in HB=BH. This short B–B distance is preserved in the lithio derivatives **7a–d** (1.457–1.552 Å, 6-31G* data). There are two isomers that correspond to minima (at 3-21G): the dibridged (folded) structure **7a** and the singly bridged perpendicular arrangement **7b**, which is higher in energy by 7.8 kcal/mol (Table III). The corresponding planar dibridged isomer **7c** is the transition structure (one imaginary frequency) for the planar inversion of **7a**. The activation energy, however, is only 1.8 kcal/mol (Table III). Similarily, **7d** is the transition structure for the conversion of **7b** into an identical form.

Lithiodiborane(4) is stable against loss of LiH (+93.3 kcal/mol, eq 9a). For computational convenience we calculated the resulting diborane(2), B_2H_2, in the singlet state ($^1\Delta_g$). The ground-state triplet ($^3\Sigma_g^-$) is calculated to be 16.6 kcal/mol lower in energy,[5] thus reducing the decomposition energy to +76.7 kcal/mol (eq 9b).

The most stable conformation of 1,2-dilithiodiborane(4) is the folded, doubly lithium bridged **8a**. The planar isomer **8b** is the transition structure for the planar inversion process of **8a** with a small activation energy, 1.0 kcal/mol. The doubly hydrogen bridged **8c** is a minimum but is higher in energy by 43.4 kcal/mol.

No-Bond–Double-Bond (Bond-Stretch) Isomerism in $Li_2B_2H_4$. Since both **4a** with its long B–B separation (4.204 Å) and **6a** with its B=B double bond (1.613 Å) are minima, the barrier separating the two structures is of interest. This provides an example of another type of "bond-stretch isomerism", which has enjoyed a revival of interest recently.[43] The interconversion process within the D_{2h} point group is "forbidden": there is no occupied π MO in **4a** corresponding to the π HOMO of **6a**. Consequently, the SCF energy curve for a D_{2h} pathway between the two minima (i.e., varying the B–B separation and reoptimizing the remaining geometrical parameters) reveals a cusp. A transition structure with symmetry reduced to C_{2h} appeared to be likely in view of the dimerization route of singlet methylene, CH_2,[44] a species isoelectronic with the singlet BH_2^- anion.[45] Within the C_{2h} point group a stationary point (**10a**) was found, but this had two imaginary vibrational modes. Further reduction of symmetry to C_s resulted in an energy lowering by 6.5 kcal/mol. However, the C_s "transition structure" **10b** still had two imaginary frequencies. The true transition structure **11** (one imaginary frequency corresponding to a B–B stretch) has *no* symmetry (C_1 point group); it is only 4.9 kcal/mol higher in energy than planar **4a**. (This value may be lower or even disappear at higher levels of theory.) The B–B separation in **11** is 2.699 Å (6-31G* data), about the average of the B–B distances in **4a** and **6a**. Due to the small activation energy for converting **4a** into the much more stable **6a**, the "no-bond isomer" **4a** should be very difficult to observe (although derivatives might be more stable).

The B–B bond order in **4a** (obtained by NPA at 3-21G) is –0.012; i.e., there is actually no B–B bonding. The formation of a B–B bond in the transition structure **11** is indicated by a bond order of 0.250, compared with 1.969 in **6a** (double bond).

Possibilities for the Synthesis of $Li_2B_2H_4$. Since **4a** with no B—B bond may be a distinct species, it could be a precursor for the synthesis of the B=B double-bonded **6a**. Chloroboranes(3) are readily available[46] as ether adducts, $ClBR_2 \cdot OR'_2$. Halogen–metal exchange by lithium should lead to $LiBR_2$, which is expected to oligomerize. Suitable substituents R may result in the formation of the dimer $(LiBR_2)_2$, corresponding to **4a**, which in turn might isomerize into a B=B double-bonded species, perhaps even spontaneously depending on the nature of the R groups. The rather low activation energy (4.9 kcal/mol for the parent system) makes this approach likely.

Another route to derivatives of **6a** might be the two-electron reduction of diborane(4) derivatives, B_2R_4, with lithium metal. The reduction of B_2R_4 (R = neopentyl) has been described by Klusik and Berndt,[19] but the reaction evidently stopped at the radical anion stage. Nevertheless, the two-electron reduction should be possible according to our calculations and seems to be a promising route to compounds exhibiting a B=B double bond. This is a challenge for experimental chemists.

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Registry No. $Li_2B_2H_4$, 116212-83-0; H_2, 1333-74-0; LiH, 7580-67-8; Li_2, 14452-59-6; BH_3, 13283-31-3; $LiBH_2$, 64360-74-3; Li_2BH, 116212-84-1; B_2H_2, 56125-74-7; B_2H_4, 18099-45-1; B_2H_6, 19287-45-7; LiB_2H_3, 98213-29-7; $Li_2B_2H_2$, 116212-85-2; $(LiBH_2)_2$, 88656-95-5; $B_2H_3^-$, 69155-47-1; $B_2H_4^{2-}$, 110892-00-7; $B_2H_4^-$, 111002-22-3.

Supplementary Material Available: Full geometry information in the form of archive entries for all calculated species (5 pages). Ordering information is given on any current masthead page.

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