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Allylborane and Its Isomers. An ab Initio Study of the C_3BH_7 Potential Energy Surface, the Barrier to 1,3-Shifts in Allylboranes, and Nonclassical Boracyclobutane, Cyclopropylborane, and Vinylborane Structures

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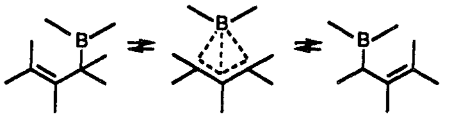
Abstract: Degenerate 1,3-BR_2-shifts in allylboranes (R = alkyl) are shown by ab initio molecular orbital theory to proceed through a nonplanar transition structure with C_s symmetry. The MP2/6-31G*//6-31G* + ZPE barrier of 9.2 kcal/mol for dimethylallylborane agrees with experimental values. However, the corresponding bridged structure (**2**) is the most stable form of the parent allylborane, $CH_2{=}CHCH_2BH_2$ at MP2/6-31G*//MP2/6-31G* + ZPE. The unsymmetrical open conformation (**1**), which prefers C_1 symmetry, is only 0.1 kcal/mol higher in energy. Other structures on the C_3BH_7 potential energy surface are also comparable in energy. Like the isoelectronic cyclobutyl cation (bicyclobutonium ion), the four-membered boron heterocycle boretane (**3a**) prefers a nonplanar structure (C_s symmetry). Another small ring isomer, cyclopropylborane with a bisected geometry, **4a**, is only 1.2 kcal/mol higher in energy than **1**. The calculated (IGLO) chemical shifts of the isomers are discussed. The boron nucleus in the symmetrically bridged allylborane **2** is calculated to be strongly shielded (−49 ppm), whereas borons incorporated in small ring systems are predicted to be deshielded (e.g., 93 ppm for **5** and 97 ppm for planar **3b**). The rotation barriers in vinylborane and dimethylvinylborane are 6.9 and 4.0 kcal/mol, respectively.

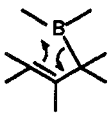
Introduction

Allylboranes are important synthetic reagents that add to, e.g., aldehydes, ketones, olefins, and acetylenes, forming new carbon–carbon bonds.[1,2] 1,3-Shifts in allylboranes occur readily; cyclic transition states are believed to be involved.



Such sigmatropic shifts of boron complicate synthesis involving unsymmetrical allylboranes, since the thermodynamically most stable isomer tends to form.[3,4]

The experimental energy barriers for such [1,3] boron migrations are in the $\Delta H^{\neq}$ = 10–15 kcal/mol range.[4–6] Kramer and Brown established that these rearrangements are intramolecular.[6] Lemal and co-workers proposed[7] that the [1,3] sigmatropic shifts of boron in allylboranes proceed through cyclically delocalized transition states. Such shifts have been designated "pseudopericyclic" because the vacant orbital at boron exchanges roles with the bonding orbitals at the boron atom.[7,8] The arrows in the representation below imply the involvement of four electrons in the delocalized transition state:



The allylborane rearrangement has been studied by PRDDO calculations.[8] A cyclic structure (cf. **2**) was found to be a transition state; the energy barrier was computed to be 11 kcal/mol relative to allylborane, $CH_2{=}CHCH_2{-}BH_2$. Our first examination of this problem at the 3-21G ab initio level a decade ago gave a similar barrier. Although these values correspond to experimental barriers for allylborane derivatives, we will show here that such apparent agreement is fortuitous and misleading.

We have now reinvestigated the [1,3] sigmatropic shift of boron by examining all relevant conformational and structural isomers of C_3BH_7 systems at high levels of ab initio theory. This extends our earlier studies of allyllithium, -sodium, and -magnesium hydrides,[9] which provide interesting comparisons. The alkali metals prefer symmetrically bridging allyl positions in contrast to the magnesium derivatives. However, the 1,3-shift barrier for the latter is only 2.8 kcal/mol (3-21G basis set).

Our second objective is to ascertain the energetic relationship between allylborane and its formal intramolecular hydroboration product, boracyclobutane, which has not yet been reported. Are the synthetic problems due to thermodynamic instability? Led by theoretical investigations,[10] experimental small-ring boron chemistry has blossomed recently.[11]

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(1) E.g.: (a) Kramer, G. W.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 2292. (b) Mikhailov, B. M. *Pure Appl. Chem.* **1983**, *55*, 1439. (c) Dittrich, K.; Bube, T.; Stürmer, R.; Hoffman, R. W. *Angew. Chem.* **1986**, *98*, 1016. (d) Yamamoto, Y.; Nishii, S.; Maruyama, K.; Komatsu, T.; Ito, W. *J. Am. Chem. Soc.* **1986**, *108*, 7778. (e) Matteson, D. S. *Synthesis* **1986**, 973. (f) Roush, W. R.; Bamfi, L.; Park, J. C.; Hoong, L. K. *Tetrahedron Lett.* **1989**, *30*, 6457.

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Table I. Total Energies of C_3H_7B Isomers (−au)

compound	ZPE[a]	HF/6-31G*[b]	MP2(FU)[c]	MP3(FC)[d]	MP4sdtq[e]
1	60.81 (0)	142.31679	142.79597	142.81128	142.83691
2	61.73 (1)	142.29645	142.79690	142.80918	142.83537
3a	62.34 (0)	142.31764	142.80019	142.81619	142.83969
3b	61.94 (1)	142.31691	142.79555	142.81447	142.83644
4a	61.92 (0)	142.31453	142.79570	142.81165	142.83470
4b	60.73 (1)	142.30288	142.78121	142.79850	142.82090
5	61.66 (0)	142.31451	142.79485	142.81362	142.83514
6	60.90 (0)	142.34052	142.81337	142.83311	142.85704
7	61.04 (0)	142.33187	142.80480	142.82316	142.84788

[a] Zero-point energies in kcal/mol; in parentheses, number of imaginary frequencies: 0 = minimum, 1 = transition state. [b] 6-31G*//6-31G*. [c] MP2(FU)/6-31G*//MP2(FU)/6-31G*. [d] MP3(FC)/6-31G*//MP2(FU)/6-31G*. [e] MP4SDTQ(FC)/6-31G*//MP2(FU)/6-31G*.

Table II. Relative Energies of C_3H_7B isomers (kcal/mol)

species	6-31G*[a]	MP2(FU)[b]	MP3(FC)[c]	MP4sdtq[d]	final[e] +ZPE
1	0.0	0.0	0.0	0.0	0.0
2	12.8	−0.6	1.3	1.0	1.8
3a	−0.5	−1.2	−3.1	−1.7	−0.9
3b	−0.1	0.3	−2.0	0.3	1.2
4a	1.4	0.2	−0.2	1.4	2.2
4b	8.7	9.3	8.0	10.0	10.1
5	1.4	0.7	−1.5	1.1	0.3
6	−14.9	−10.6	−13.7	−12.6	−12.5
7	−9.5	−5.5	−7.5	−6.9	−6.7

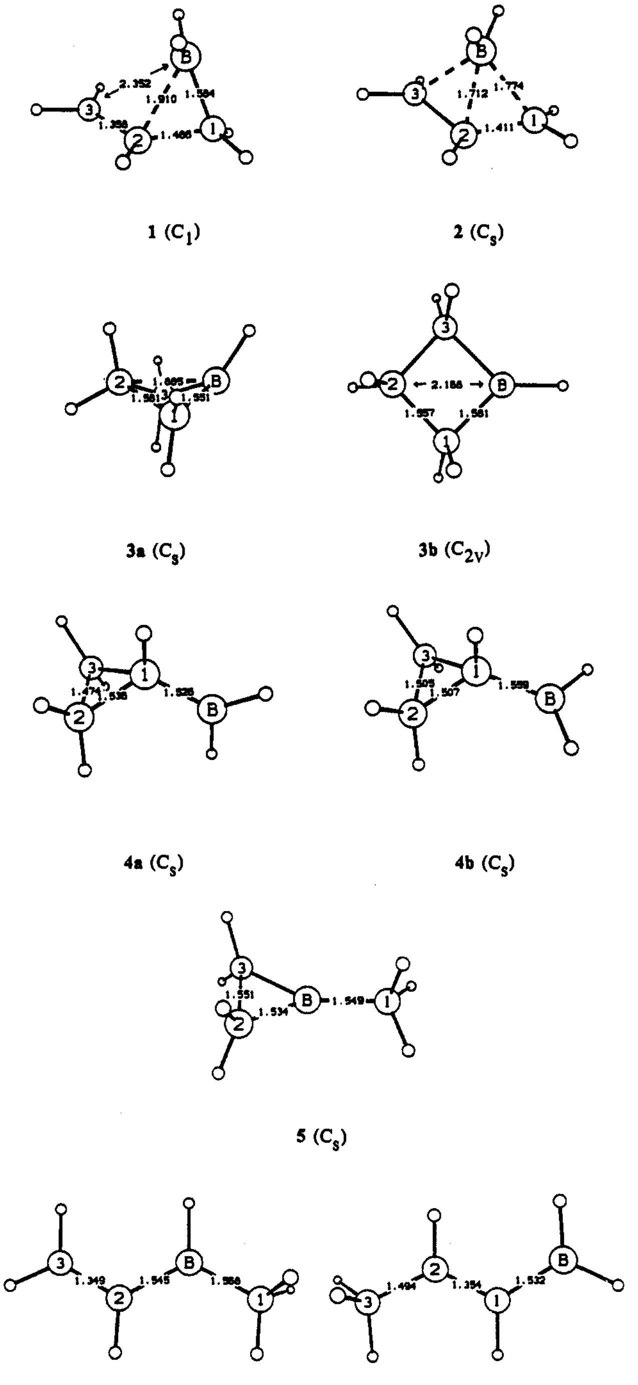
[a] 6-31G*//6-31G*. [b] MP2(FU)/6-31G*//MP2(FU)/6-31*. [c] MP3(FC)/6-31G*//MP2(FU)/6-31G*. [d] MP4SDTQ(FC)/6-31G*//MP2(FU)/6-31G*. [e] MP4/6-31G*//MP2/6-31G* relative energies corrected for zero-point energies (scaled by 0.89).

A further impetus is to compare the C_3BH_7 isomers with the well-known isoelectronic $C_4H_7^+$ cations, e.g., cyclopropylcarbinyl, homoallyl, cyclobutyl, and methylallyl.[12] Hence, cyclopropylborane[13] in both bisected and perpendicular conformations as well as methylvinylborane, 1-propenylborane, and 1-methylborirane (1-methylboracyclopropane) are included in the present study.

Since the calculated 1,3-shift barrier for the parent system, allylborane, turns out to be negligible, we examined the effects of methyl substituents on boron. The 1,3-shift barrier calculated for dimethylallylborane agrees satisfactorily with experiment. Dimethylallylborane is also a more realistic model system since the various C_3BH_7 isomers containing BH bonds should dimerize readily.

Methods

The calculations employed the GAUSSIAN 82 and 88[14] and CADPAC[15] programs. The geometries were fully optimized with the 6-31G* basis set,[16] and the nature of each stationary point was characterized by a frequency calculation at that level. In addition, most of the species were also optimized at the correlated MP2(Full)/6-31G* level (MP2(FU)/6-31G*//MP2(FU)/6-31G*), followed by single-point calculations at the MP4SDTQ/6-31G* level in the frozen core approximation (MP4SDTQ(FC)/6-31G*//MP2(FU)/6-31G*). The absolute energies of all C_3BH_7 isomers investigated are summarized in Table I. Table II gives the relative energies at the various theoretical levels. The final values (MP4SDTQ/6-31G*//MP2/6-31G* + ZPE) have been corrected for the 6-31G* zero-point energy (ZPE) differences, scaled by 0.89.[16] The MP2/6-31G*//6-31G* + ZPE level sufficed for the larger dimethylallylborane; data are given in Table III. The MP2/6-31G* geometries are shown in Figure 1.



1 (C_1)

2 (C_s)

3a (C_s)

3b (C_{2v})

4a (C_s)

4b (C_s)

5 (C_s)

6 (C_s)

7 (C_s)

Figure 1. MP2/6-31G* optimized geometries of the C_3H_7B isomers **1–7**.

The chemical shifts were calculated using the IGLO (individual gauge for localized orbitals) method.[17,18] Basis sets of triple zeta + polarization

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[12] (a) Saunders, M.; Laidig, K.; Wiberg, K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652. (b) Koch, W.; Liu, B.; DeFrees, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 7325.

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[16] Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

Table III. Absolute (–au) and Relative (kcal/mol) Energies of Dimethylallylboranes

point group	species	ZPE (6-31G*)	6-31G*[a]	MP2/6-31G*[b]	6-31G*[a]	MP2/6-31G*[b]	final +ZPE[c]
8a	C_1	98.78 (0)	220.41455	221.16487	0.0	0.0	0.0
8b	C_s	99.39 (1)	220.37645	221.15114	25.8	8.6	9.2

[a] 6-31G*//6-31G*. [b] MP2(FU)/6-31G*//6-31G*. [c] MP2/6-31G*//6-31G* relative energies with zero point corrections (ZPE's scaled by 0.89).

Table IV. IGLO ^{11}B[a] and ^{13}C[b] Chemical Shifts of C_3H_7B Isomers[c] (in ppm)

species	B	C(1)	C(2)	C(3)
1	1.3	17.5	127.4	117.4
8a[d]	81.8	27.5	135.4	112.8
Expt B(CH₂CH=CH₂)₃[e]	*80.2*	*34.8*	*131.8*	*114.8*
2	−48.5	55.1	121.4	
3a	50.3	24.6	−10.3	
3b	96.9	16.7	15.4	
4a	77.6	1.7	2.3	
Expt c-PrBMe₂[f]	*81.8*			
Expt c-PrBF₂[g]			*4.7*	
4b	82.4	−3.2	−2.9	
5	93.4	0.6	−10.2	
6	72.4	5.5	145.5	157.4
Expt H₂C=CHBMe₂[h]	*74.5*	*11.6*	*144.6*	*135.8*
7	67.4	136.6	178.2	18.5

[a] Relative to $BF_3 \cdot OEt_2$. [b] Relative to TMS. [c] Numbering as in Figure 1. [d] II′//6-31G* level. [e] Reference 25. Michailov, B. M.; Negrebetskii, V. S.; Bogdanov, A. V.; Kessenikh, A. V.; Bubnov, Y. N.; Baryshnikova, T. K.; Smirnov, V. N. *Zh. Obshch. Khim.* **1974**, *44*, 1878. [f] Reference 22. [g] Reference 21. [h] Reference 24a; reference 29.

(TZP) quality for boron and carbon and of double zeta (DZ) quality for hydrogen (designated II′) were used employing the MP2/6-31G* geometries.

Results and Discussion

Allylboranes 1 and 2. The most stable open geometry of allylborane is unsymmetrical **1** (C_1 point group), but a bridged form **2** with C_s symmetry is of comparable stability. The calculated relative energy of **1** and **2** depends strongly on the theoretical level employed (Table II). At HF/6-31G*, **2** is a transition state for the interconversion of **1** and its degenerate counterpart with a barrier of 12.8 kcal/mol. (This value corresponds to the PRDDO[8] and to our earlier 3-21G results.) However, at the correlated MP2/6-31G* level, **2** is even slightly more stable than **1**, suggesting both to be minima with similar energies. Higher correlation levels and the inclusion of zero-point correction slightly favor **1**, and our final estimate for the barrier in the parent allylborane system is 1.8 kcal/mol. Hence, the apparent agreement of the experimental 1,3-shift barrier with that calculated with PRDDO and at Hartree–Fock levels for the parent compound is coincidental.

Dimethylallylborane (**8**) should be a more realistic model for the experimentally relevant, substituted species.[1,2] Because of size limitations, the geometries of unsymmetric **8a** and symmetric **8b** were only optimized at 6-31G* (Figure 2). Frequency calculations at this level also showed **8a** to be a minimum and **8b** to be a transition state. While the HF/6-31G* barrier is 25.8 kcal/mol (Table III), inclusion of electron correlation (MP2/6-31G*//6-31G*) and zero-point correction reduces this to 9.2 kcal/mol. This value is at the lower limit of the barriers found experimentally (10–15 kcal/mol).

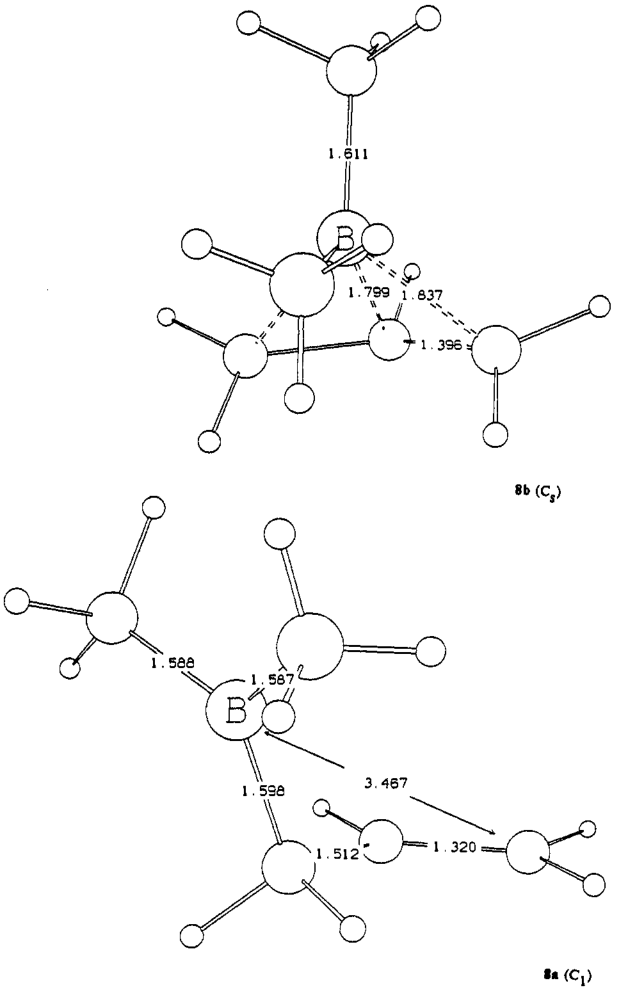

Figure 2. 6-31G* optimized geometries of dimethylallylborane **8a** and **8b**.

Why is the 1,3-shift barrier so susceptible to substituents? Methyl groups stabilize three-coordinate boron (see below). The hyperconjugative contribution to this stabilization is of little importance for the pentacoordinate boron in the cyclic forms, **2** and **8b**, since no vacant p-orbitals are available. The bonding in **2** with its five-coordinated boron resembles the situation in the polyhedral boron compounds and is reflected in the calculated ^{11}B chemical shift for **2** of −49 ppm (Table IV). Since hyperconjugation is less important in **8b**, the $B–CH_3$ distances are 0.02 Å longer than in **8a**.

In **1**, the rather small CCB angle (76.9° at MP2/6-31G*), the short C(2)B distance (1.910 Å), and the twisting of the BH_2 group result from intramolecular interactions between the vacant boron p-orbital and the π-electrons of the double bond.[20] This is shown by the significant BC bond order (Wiberg's definition[19]) of about 0.22 between boron and both of the olefinic carbons.

In addition to **1** (and **2**), three other allylborane conformers were investigated, in which the boron atoms were constrained to lie in the C(1)C(2)C(3) plane and C_s symmetry was imposed:

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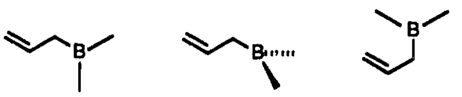
(19) Wiberg, K. *Tetrahedron* **1968**, *24*, 1083.

(20) Intermolecular olefin–BH_3 complexes have been studied with reference to the mechanism of the hydroboration reaction; see, e.g.: (a) Clark, T.; Wilhelm, D.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Comm.* **1983**, 606. (b) Hommes, N. J. R. v. E.; Kaneti, J.; Schleyer, P. v. R., *J. Org. Chem.* In press.

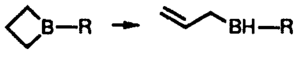


As these structures all were somewhat less stable than **1** at MP2/6-31G*//3-21G, they were not refined at higher levels. These geometries preclude boron π-olefin interactions.

Cyclic C_3H_7B Structures, 3–5. The nonplanar bending of boracyclobutane (**3a**) is substantial. The puckering angle, C(2)C(1)C(3)B (126.9° at the MP2/6-31G* level), facilitates transannular interaction (the C(2)B distance is 1.885 Å). Inversion through a planar C_{2v} transition state (**3b**) with a C(2)B distance of 2.168 Å requires 2.5 kcal/mol. The inversion barrier of the isoelectronic bicyclobutonium ion (**9**) is considerably higher, 16.1 kcal/mol.[12] The bridged allylborane **2** also is isostructural with **9**; in this case, the "opposite" carbon, C(3), is replaced by boron. However, **3a** is more stable than **2** by 2.7 kcal/mol.

As far as we are aware, no derivatives of boracyclobutane are known experimentally. The relative energies in Table I suggest that **3a** is not disfavored energetically; the ring opening to allylborane **1** is calculated to be endothermic by 0.9 kcal/mol (entropy, however, favors ring-opened forms). Since **3a** itself is expected to dimerize readily through BH bridging, only substituted forms are conceivable as monomers experimentally. However, (e.g., alkyl-) substituted **2** may take advantage of two (hyperconjugatively) stabilizing interactions, whereas in a substituted **3a** only one of these is possible. Hence, allylborane derivatives with an additional substituent on boron may be more stable than boracyclobutane derivatives.

The effect of one substituent on the relative energies on **1** and **3a** is relatively small. The enthalpies for the reactions



are 2.2, 4.4, and 2.5 kcal/mol for R = H (i.e., **3a** → **2**), CH_3, and NH_2, respectively (MP2/6-31G*//6-31G* + ZPE level; the value for R = H in Table I refers to the MP2 optimized geometries). Amino substituents, commonly used in synthetic boron chemistry, therefore are not expected to stabilize boracyclobutanes. However, the effect of the substituents on the geometry of the four-membered ring is quite interesting. When electron-donating substituents are present, the nonclassical transannular 1,3-interaction becomes less important; the C(2)B distances increase progressively from 1.885 Å in **3a** (R = H) to 1.993 Å (R = CH_3) and to 2.095 Å (R = NH_2); see Figure 4. The last derivative is nearly planar (cf. **3b**).

The bisected conformation of cyclopropylborane, **4a**, is known to have a lower energy than the perpendicular isomer **4b**,[13,21] the transition structure for the rotation of the BH_2 group. Our final energy difference is 7.9 kcal/mol. However, an experimental upper limit of ca. 3 kcal/mol for this rotational barrier has been given for the additionally stabilized dimethylcyclopropylborane.[22] The MP2/6-31G* fully optimized geometries in Figure 1 show the different degrees of hyperconjugative involvement of the "vacant" B p-orbital and the three-membered rings.[13] The C–B bond is shortened by 0.033 Å in **4a**, and the distal and vicinal CC ring bonds have different lengths (1.474 and 1.536 Å, respectively).

Despite its large angle strain, methylborirane (**5**) is only 0.3 kcal higher in energy than allylborane **1**. However, **5** benefits from hyperconjugative stabilization, which is reflected, e.g., in the comparatively short ring–CB distances of 1.534 Å (the geometries of substituted boriranes have been analyzed[10c]). But unlike the isoelectronic cyclopropyl cations that readily open to give allyl cations exothermically, methylborirane is expected to be isolable. While the isomeric methylvinylborane **6** is more stable by 12.8 kcal/mol, disrotatory ring opening of **5** would lead directly to the unstable $CH_2B(CH_3)CH_2$ isomer. The latter is 27.5 kcal/mol less stable than **5** at MP2/6-31G*//MP2/6-31G* + ZPE. Substituted derivatives of **5** (with bulky *tert*-butyl and $SiMe_3$ groups on boron and carbon, respectively) already have been prepared.[11b,e]

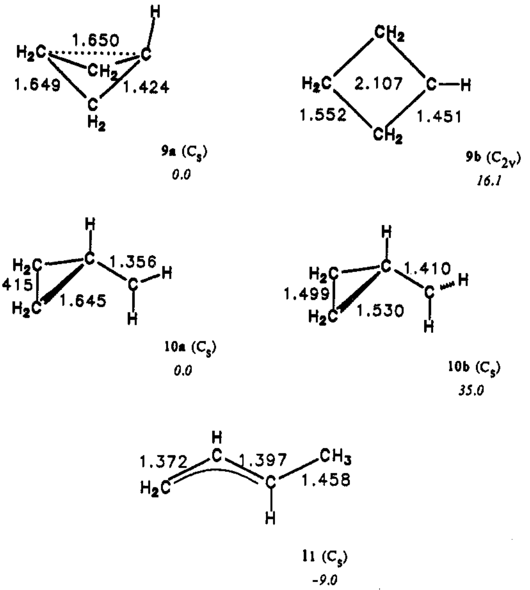


Figure 3. MP2/6-31G* optimized geometries of $C_4H_7^+$ isomers **9–11** (from ref 12). In italics: relative energies at the MP4sdtq/6-31G*//MP2/6-31G* level (**10b**: MP3/6-31G*//MP2/6-31G*; **11**: MP4sdtq/6-31G**//MP2/6-31G**).

Vinylboranes 6 and 7. The relative energy of methylvinylborane **6** versus 1-propenylborane **7** (eq 1) illustrates the stabilizing effect of boron-attached alkyl groups mentioned above. Although the olefin moiety in **7** is more highly substituted, **6** is more stable by 5.8 kcal/mol. This value represents a rough estimate for the stabilization of a three-coordinate boron by one methyl group to which hyperconjugation contributes, but part of this is due to the differences in the CC versus CB σ-bond energies in the absence of hyperconjugation.

$$\underset{\mathbf{7}}{CH_3CH{=}CHBH_2} \rightarrow \underset{\mathbf{6}}{CH_2{=}CHBHCH_3}, -5.8\ \text{kcal/mol} \quad (1)$$

$$CH_3CH_2BH_2 \rightarrow CH_3BHCH_3, -12.0\ \text{kcal/mol} \quad (2)$$

$$CH_3BH_3^- + BH_3 \rightarrow CH_3BH_2 + BH_4^-, -6.1\ \text{kcal/mol} \quad (3)$$

The similar isomerization reaction (eq 2) is more exothermic than eq 1, but suffers from the same shortcomings. Perhaps the best estimate by the hyperconjugative stabilization of the CH_3 group in CH_3BH_2 (6.1 kcal/mol) is provided by the isodesmic equation 3. The problem of disecting σ- and π-substituent effects in boron compounds has been discussed.[10c]

Comparison with $C_4H_7^+$. The potential energy surface (PES) of $C_4H_7^+$ has been investigated at high levels of theory.[12] Geometries and relative energies of the isomers directly related to C_3BH_7 species of this study are given in Figure 3. In general, the same effects discussed for the boron compounds are found in the analogous carbocations, but are larger in magnitude. E.g., in the bicyclobutonium ion **9a**, the transannular 1,3-interaction is stronger; the C(2)C(3) distance of 1.649 Å is considerably longer than the corresponding CC bond length in **3a** (1.581 Å), and the barrier of inversion proceeding through **9b** is higher (16.1 kcal/mol; **3**, 2.1 kcal/mol).

The involvement of the cyclopropane Walsh orbitals is more pronounced in the bisected cyclopropylcarbinyl cation **10a** than in **4a**.[10c] This is reflected in the larger asymmetry of the ring CC distances. In **10a**, the difference between the long bonds and the short bond is 0.230 Å; in **4a**, this difference is 0.062 Å. In addition, the $-CH_2^+$ rotation barrier proceeding through perpendicular **10b**, 35 kcal/mol, is considerably higher than that in the boron analogue (7.9 kcal/mol, **4a** versus **4b**).

As is the case with its isoelectronic C_3BH_7 analogue **6**, the 1-methylallylcation **11** is the global minimum on the $C_4H_7^+$ po-

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(21) Odom, J. D.; Szafran, Z.; Hohnston, S. A.; Li, Y. S.; Durig, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 7173.

(22) Cowley, A. H.; Furtsch, T. A. *J. Am. Chem. Soc.* **1969**, *91*, 39.

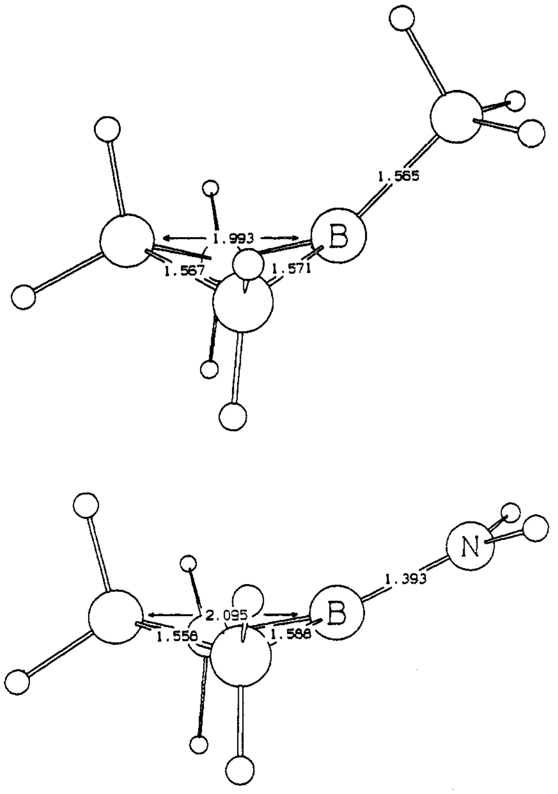


Figure 4. MP2/6-31G* optimized geometries of methyl- and amino-substituted boracyclobutane. The geometry of the amino derivative is almost classical (cf. **3b** in Figure 1).

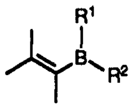
tential energy surface (PES).[12b] The energy differences are similar here: **6** is more stable than **3a** by 11.6 kcal/mol while **11** is 9.0 kcal/mol lower in energy than **9a**.

The calculated PES for $C_4H_7^+$ is much more susceptible to the level of theory, especially to inclusion of electron correlation, than the C_3BH_7 PES. The relative energies of the various isomers are strongly dependent on the level employed. Furthermore, the nature of the stationary points sometimes changes at correlated levels; e.g., **10a** is not a minimum at the HF/6-31G*, but only at the MP2/6-31G** level. For the C_3BH_7 PES this sensitivity is much less pronounced. Except for the bridged allylborane **2**, the calculated relative energies in Table II show only minor changes with the theoretical levels.

Chemical Shifts. It has recently become possible to calculate ab initio NMR chemical shifts with remarkable accuracy.[23] We applied the IGLO (individual gauge for localized orbitals) method[17,18] to the species studied here. The δ ^{11}B and ^{13}C values, calculated with a basis of triple zeta plus polarization quality on MP2/6-31G* geometries (notation II′//MP2/6-31G*), are summarized in Table IV.

The ^{11}B chemical shifts of the allylboranes **1** and **2** are the most shielded among the C_3BH_7 isomers. δ ^{11}B for symmetrically bridged **2**, −48.5 ppm, is in the range expected for pentacoordinate boron.[24] But the formally three-coordinate boron in **1** also is shielded considerably (δ ^{11}B = 1.3 ppm) due to the interaction with the π-electrons of the double bond. The experimental values lie in the "normal" range near ca. 80 ppm (e.g., tris(allyl)boron: 80.2 ppm[25]). Here, the influence of the substituents is dramatic; for dimethylallylborane, a δ ^{11}B value of 81.8 ppm is computed (II′//6-31G*). This compares excellently with the experimental chemical shifts (Table IV).

Table V. Computed Geometries[a] (MP2/6-31G*) and Chemical Shifts[b] (IGLO II′//MP2/6-31G*) of Vinylboranes



					δ ^{11}B, ^{13}C		
R¹	R²		$C_\alpha C_\beta$	$C_\beta B$	B	C_α	C_β
H	H		1.351	1.539	68.9	143.0	160.6
H	Me	(**6**)	1.349	1.545	72.4	145.5	157.4
Me	Me	(**12**)	1.348	1.559	73.0	143.6	146.6
Me	*Me*	*(expt)*[c]			*74.5*	*144.6*	*135.8*

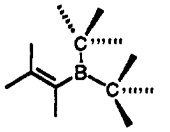
[a] Bond distances in Å. [b] In ppm relative to $BF_3 \cdot OEt_2$ or TMS. [c] Reference 24a.

The δ ^{11}B of planar **3b** is calculated to be deshielded considerably (96.6 ppm). This is in accord with the downfield shift observed in cyclic alkylboranes (e.g., methylboracyclohexane, 86.0 ppm;[26] methylboracyclopentane, 92.5 ppm[24]). The transannular interaction in puckered **3a** results in a shift to higher field (50.3 ppm). However, in a methyl-substituted boracyclobutane, this interaction is reduced, and a chemical shift of 70.3 ppm is predicted (II//MP2/6-31G*). The strong π-donation of an amino substituent, which is responsible for the nearly "classical" character of this derivative, is reflected in the computed δ ^{11}B value of 48.9 ppm, which is even more shielded than in nonclassical **3a**.

The ^{11}B chemical shift of perpendicular **4b**, 82.4 ppm, is in the usual range of three-coordinate alkylboranes;[24] δ ^{11}B of bisected **4a**, 77.6 ppm, is shifted slightly to higher field. The boron in methylborirane **5** (δ 93.4 ppm) is somewhat deshielded with respect to normal trialkyl boranes. The boron chemical shifts of **6** and **7**, 72.4 and 67.4 ppm, respectively, are in the usual range expected for vinylboranes (around 70 ppm).[24]

The ^{13}C chemical shifts for most of the isomers are in the regions expected for the types of carbons involved.[27] C(2) in boracyclobutane **4a** is somewhat shielded (−10.3 ppm), but may be compared to the analogous carbon in the methylcyclobutonium cation (−3.0 ppm).[28] The shielding of the ring carbons in the hypothetical methylborirane (−10.2 ppm) is quite unusual.

The vinylic β-carbon chemical shift calculated for monomethylvinylborane **6** (157.4 ppm) differs substantially from the reported value for dimethylvinylborane (135.8 ppm).[29] Puzzled by this deviation, we optimized dimethylvinylborane, **12**,



12

which was found to possess C_1 symmetry: Unlike early semiempirical level predictions,[30] all nonhydrogen atoms lie essentially in a plane. The orientation of the methyl hydrogens resembles that in dimethylborane which possesses C_2 symmetry,[31] as does the isoelectronic 2-propyl cation.[32] But as in the latter case, the methyl group rotation barrier for **12** is very small (0.2 kcal/mol at MP2/6-31G*//MP2/6-31G* + ZPE) implying virtually free rotation of the methyl groups. For **12**, the barrier of vinyl group rotation around the BC bond is computed to be 4.0 kcal/mol (same level); this is somewhat smaller than that for the parent compound, vinylborane (6.9 kcal/mol). Experimentally, in upper limit of ca. 8 kcal/mol has been estimated for **12**. The analogous barriers

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[23] Review: Chestnut, D. B. *Annu. Rep. NMR Spectrosc.* **1989**, *21*, 51.

[24] See, e.g.: (a) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds.* In *NMR, Basic Principles and Progress*; Diehl, P., Fluck, E., Kosteld, R., Eds. Springer: Berlin, Heidelberg, 1978. (b) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 61 and references cited therein.

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[27] See, e.g.: Kalinowski, H. O.; Berger, S.; Braun, S. *^{13}C NMR Spectroscopy*; Wiley: New York, 1988.

[28] Siehl, H. U. *J. Am. Chem. Soc.* **1985**, *107*, 3390.

[29] Odom, J. D.; Moore, T. F.; Johnston, S. A.; Durig, J. P. *J. Mol. Struct.* **1979**, *54*, 49.

[30] Allinger, N. L.; Siefert, J. S. *J. Am. Chem. Soc.* **1975**, *97*, 752.

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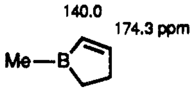
for the CC bond rotations in the allyl cation[33] and 1,1,2-trimethylallyl cation,[34] 34.9 and 11.7 kcal/mol, respectively, indicate that the conjugative overlap between the π-electrons and the vacant boron p-orbital in the vinylboranes is significantly smaller.

Table V summarizes the computed geometries and chemical shifts for methyl-substituted vinylboranes. The introduction of the second methyl group in **12** strongly affects the chemical shift of the vinylic β-carbon, which is shielded by more than 10 ppm with respect to the monomethyl derivative **6**. However, the δ ^{13}C chemical shift computed for C_β of **12**, 146.6 ppm, still shows an unusually large deviation from the experimental value (135.8 ppm). Obviously, δ $^{13}C_\beta$ is rather susceptible to perturbations of the π-electron distribution induced by substituents. E.g., attachment of an alkyl substituent to the β-carbon results in a downfield shift for δ ^{13}C; see **7** in Table IV, 178.2 ppm; a comparable experimental example may be methyl-2-borolene:[35]



Conclusions

The barrier for the [1,3] sigmatropic boron shift in dialkylallylboranes is reasonably well-described by theory, but the alkyl groups on boron have an important influence. The parent allylborane would be expected to have greater fluxional character (with a barrier less than 2 kcal/mol). Cyclic isomers with nonclassical structures (e.g., **2**) may actually be favored.

A comparison of other chemically relevant C_3BH_7 isomers to their isoelectronic $C_4H_7^+$ counterparts generally reveals the same structural influences to be important for both classes of compounds. However, the electronic effects are larger in magnitude for the carbocations, as reflected in a higher inversion barrier for the bicyclobutonium ion and the higher rotation barrier for the cyclopropylcarbinyl cation (relative to their boron counterparts).

The NMR chemical shifts we predicted at an adequate level of sophistication (IGLO TZP basis set for MP2/6-31G* geometries) should be reliable. Comparison with experimentally accessible derivatives usually gives a good agreement of theory and experiment. One exception is the ^{13}C chemical shift of the vinylic β-carbon in vinylboranes which proves to be very sensitive to the influence of directly bound and remote substituents.

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Elucidation of the Conformational Properties of *N*-Formylglycine Dithio Acid by ab Initio SCF-MO Calculations

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Abstract: Ab initio SCF-MO calculations were carried out for the molecule *N*-formylglycine dithio acid using STO-3G and 3-21G basis sets. Structures and energies of several conformations of this molecule determined by gradient geometry refinement are reported, and some conformationally dependent local geometry trends discussed. For conformations involving rotational isomerism about the NH—CH_2 and CH_2—C(=S) single bonds, the 3-21G results reveal the presence of three conformational states. These conformers are strikingly similar to those determined for glycine dithio esters by X-ray crystallographic and vibrational spectroscopic analyses. One conformer has a small NH-CH_2-C-$S_{(thiol)}$ torsional angle and close N-to-$S_{(thiol)}$ atom contact. The calculations provide a description of this N···S nonbonded interaction which has implications for the structure and reactivity of enzyme–substrate complexes which incorporate a similar contact. However, no evidence is found for favorable N-to-$S_{(thiono)}$ interactions for the conformer which has a small NH—CH_2—C=S torsional angle.

Introduction

Resonance Raman (RR) spectroscopy can provide the vibrational spectrum associated with the bonds undergoing catalytic transformation in enzyme–substrate complexes of the type RC(=O)NHCHR′C(=S)S–enzyme, where the enzyme is a member of the cysteine protease family.[1-3] For this kind of reaction intermediate, the chromophore used to generate the RR spectrum is based on the dithio group, —C(=S)S—. Obtaining the maximum amount of chemical information from the RR data requires a detailed knowledge of the interrelationship between RR spectral features and conformational states within the —C(=O)NHCHR′C(=S)SCH_2— moiety. Thus, conformational analysis of model compounds, e.g., glycine-based (R′= H) dithio esters and acids, and the setting up of spectra–structure correlations has gone hand in hand with RR studies of the enzyme complexes. Conformational analysis of the "model" dithio esters has been undertaken with use of IR, Raman, and RR vibrational

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