

In the gas phase, size effects (e.g., polarization) influence the stability of charged molecules. Thus, a comparison of a $C_7H_{11}^+$ with a $C_3H_7^+$ species (eq 1) is less appropriate than that with a secondary C_7 cation.²⁵ E.g., for the 4-heptyl cation, Bowen and Williams²⁶ have suggested a correction of 6 kcal/mol. The size-corrected "extra stabilization" of the 2-norbornyl cation relative to classical secondary counterparts, 14–19 kcal/mol, agrees with that derived from Figure 1 and with many literature estimates.^{5–13} The value in solution is 5–8 kcal/mol.^{5,8a,27}

Conclusion. The symmetrically bridged (C_s) 2-norbornyl cation structure is expected to be the only minimum on the potential energy surface. As no minima with C_1 symmetry are found, "classical" and partially bridged 2-norbornyl cations are not expected to exist at least as isolated (gas phase) entities. The extra stabilization due to bridging of the C_s 2-norbornyl cation (the "classical–nonclassical energy difference") is estimated approximately in two ways to be about 15 kcal/mol.

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Registry No. 2-Norbornyl cation, 24321-81-1.

Supplementary Material Available: Table of computed total energies at different levels (1 page). Ordering information is given on any current masthead page.

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Theoretical Structure of the $B_2H_7^-$ Anion

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The X-ray structure of $[(Ph_3P)_2N]^+B_2H_7^- \cdot CH_2Cl_2$ indicated a bent B–H–B three-center two-electron bond ($\angle BHB = 136 \pm 4^\circ$) for the $B_2H_7^-$ anion and C_s symmetry.¹ Earlier theoretical studies on isolated $B_2H_7^-$ correctly predicted that double- or triple-bridged alternatives would be less stable, but indicated that a linear single B–H–B bridge should be favored.^{2–4} The bent experimental $B_2H_7^-$ structure (1) also contrasts with the results of an X-ray structure of the related $(CH_3)_3Al-H-Al(CH_3)_3^-$ anion⁶ and with theoretical calculations on $H_3Al-H-AlH_3^-$ ⁷ which

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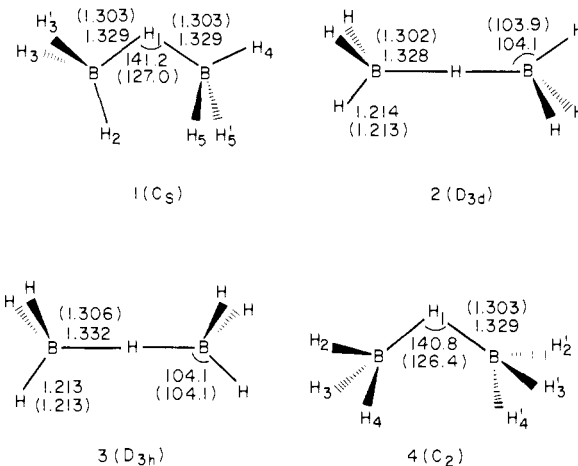


Figure 1. The various structures for $B_2H_7^-$ considered in this study. Some geometrical parameters optimized at HF/6-31G* (MP2/6-31G*) levels are shown. The remaining geometrical parameters are specified in the footnote to Table I.

all indicate linear Al–H–Al bridging to be preferred. Shore, Bau, et al. recognized that the conformation of $B_2H_7^-$ "might be sensitive to crystal lattice effects" and further X-ray and neutron diffraction experiments are being carried out.

As our previous ab initio calculations on $B_2H_7^-$, like those in the literature,^{2–4} appeared to favor a linear D_{3d} structure, **2** (the D_{3h} from **3** is only slightly less stable),⁵ we were intrigued by the apparent discrepancy with experiment. For example, when the experimental geometry **1** was taken as the starting point for optimization with the split valence 3-21G basis set,⁸ no bent minimum was found and **2** resulted. However, our prior experience with the isoelectronic $C_2H_7^+$ cation indicated such structural details to be extremely sensitive to the level of theory employed.⁹ Larger basis sets with polarization functions and especially corrections for the effects of electron correlation favor bent over linear C–H–C bridges. Thus, definitive studies on $B_2H_7^-$ need a similar degree of sophistication, which was not employed in the prior theoretical investigations.^{2–5} We now report the results of such an examination which confirms bent B–H–B structures to be favored.

Starting again with the experimental geometry of **1**, optimization was carried out at two higher levels. We first employed the 6-31G* basis set,¹⁰ which has d-type polarization functions on boron. A bent structure (see Figure 1) with a B–H₁–B angle of 141.2° was found with C_s symmetry (**1**). However, **1** had one negative eigenvalue of the force constant matrix and was a transition structure rather than a local minimum. Although having almost identical energy, a minimum, **4**, with C_2 symmetry, was located. At this level, the potential energy surface was very flat and the energies of **1** and **4** were less than a kcal/mol more stable than those of the linear alternatives, **2** and **3** (Table I). These forms had more than one negative eigenvalue of the force constant matrix¹⁴ suggesting that they are higher order saddle points.

The next geometry optimization was carried out at the MP2/6-31G* level which includes corrections for electron correlation using second-order Møller–Plesset perturbation theory.¹¹ As in the case of $C_2H_7^+$,⁹ this caused a further bending of the molecule. A B–H₁–B angle of 126.4° resulted for **4** (C_2). At this optimized MP2/6-31G* level, the energetic advantage of **4** over the linear D_{3d} (**2**) and D_{3h} (**3**) forms was still low, ≈ 2 kcal/mol. The structures of **2** and **3** reoptimized at the MP2 level underwent only minor changes.

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Table I. Energies of $B_2H_7^-$ and Related Species^a

species	optimization level			MP4/6-31G**// MP2/6-31G*	zero-point ^c energy	relative energy
	3-21G	6-31G*	MP2/6-31G*			
$B_2H_7^-$						
1 (C_s) ^e	no minimum	-53.39731	-53.59131	-53.69373	43.5 ^d	0
2 (D_{3d})	-53.09545	-53.39661 ^b	-53.58792	-53.69055	43.1 ^d	1.6
3 (D_{3h})	-53.09493	-53.39601 ^b	-53.58710	-53.68968	42.9 ^d	2.0
4 (C_2) ^f	no minimum	-53.39732	-53.59138	-53.69379	43.5	0
$BH_3 + BH_4^-$	-53.05025	-53.35511	-53.53100	-53.63125	39.7	35.4
BH_3 (D_{3h})	-26.23730	-26.39001 ^b	-26.46424	-26.50751	17.4	
BH_4^- (T_d)	-26.81295	-26.96510 ^b	-27.06676	-27.12374	22.3	

^a Absolute energies in hartrees and relative energies in kcal/mol. ^b Reference 5. ^c Calculated at the HF/6-31G* level. ^d The imaginary frequencies were also included in the zero-point energy evaluations to facilitate direct comparisons. ^e The calculated HF/6-31G* (MP2/6-31G*) geometrical parameters not specified in the figure (bond lengths in angstroms, bond angles in degrees) are $H_2-B = 1.209$ (1.206), $H_3-B = 1.216$ (1.217), $H_4-B = 1.219$ (1.221), $H_5-B = 1.212$ (1.210), $H_2-B-H_1 = 110.1$ (114.7), $H_3-B-H_1 = 101.7$ (100.1), $H_4-B-H_1 = 98.8$ (94.7), $H_5-B-H_1 = 107.3$ (109.9), $H_3-B-H_3' = 113.6$ (113.2), $H_5-B-H_5' = 114.6$ (114.8). ^f The calculated HF/6-31G* (MP2/6-31G*) geometrical parameters not specified in the figure (bond lengths in angstroms, bond angles and dihedral angles in degrees) are $H_2-B = 1.218$ (1.220), $H_3-B = 1.214$ (1.213), $H_4-B = 1.210$ (1.208), $H_2-B-H_1 = 99.5$ (95.9), $H_3-B-H_1 = 104.7$ (105.7), $H_4-B-H_1 = 109.3$ (113.2), $H_2-B-H_1-B = 152.4$ (153.6), $H_3-B-H_1-H_2 = 117.6$ (115.9), $H_4-B-H_1-H_2 = -119.4$ (-118.1).

There are two remaining factors that might influence the calculated geometries, viz., the effect of p-type polarization functions on hydrogen and the higher order effects of electron correlation.¹² Both factors were considered to a limited extent. The effect of p functions on hydrogen was probed by performing a complete geometry optimization of **4** with the larger 6-13G** basis¹⁰ at the Hartree-Fock level.¹⁵ All the parameters changed insignificantly from their 6-31G* values with the exception of the B-H₁-B angle, which decreased from 140.8° to 136.7°. The higher order effects of electron correlation were examined by optimizing the angle B-H₁-B at the third-order perturbation MP3/6-31G* level,¹¹ all the other parameters being fixed at their respective MP2/6-31G* values. The B-H₁-B angle changed only slightly, from 126.4° to 126.7°. Considering the flatness of the bending potential energy surface, the changes in the geometry due to both these effects are fairly small.

While we confirm the experimental conclusion that $B_2H_7^-$ prefers a bent structure, many geometrical details are not in good agreement. While the experimental B-H₁-B angle, 136(4)° lies between our values, the B-H₁ distances to the bridging hydrogen, 1.27 (5) and 1.00 (5) Å, are shorter than our calculated values, 1.328-1.303 Å; this is also true of the other B-H distances and the various angles. Even in **1**, where the B-H₁ distances must be nonequivalent, nearly identical values were calculated. The MP2/6-31G* B-B distance (2.33 Å) is larger than the X-ray value (2.11 Å), but in view of the flatness of the potential energy surface and the influence of the counterion and the crystal lattice, this difference is not particularly significant. Especially in such instances, the structure of isolated species may be expected to differ from those in condensed phases. Nevertheless, it is hoped that the planned neutron diffraction study will provide more accurate experimental parameters for comparison.

The minimum binding energy of BH_3 with BH_4^- has been experimentally measured to be -31 ± 8 kcal/mol in the solid phase.¹³ Previous calculations have obtained values of -21 kcal/mol^{2,3} (after applying a 4 kcal/mol correction for the neglected zero-point effects) at the Hartree-Fock level and -24 kcal/mol³ using an approximate CEPA scheme. We have calculated the final energy differences (last column, Table I) at the MP2/6-31G* geometries by including zero-point corrections and higher order electron correlation effects by means of complete fourth-order perturbation MP4 level¹¹ with the 6-31G** basis.

(12) Diffuse functions, although important for anions with lone pairs (Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609), do not improve the description of species like BH_4^- (Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, in press) and $B_2H_7^-$ (present work) significantly.

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(14) **2** and **3** respectively had 2 and 3 negative eigenvalues of the force constant matrix.

(15) A similar 6-31G** optimization of **1** has been recently performed. See: Sapsee, A.-M.; Osorio, L. *Inorg. Chem.*, submitted for publication.

The calculated binding energy (35.4 kcal/mol) is higher than the previous calculated values and is in good agreement with the experimental value.

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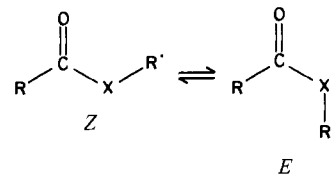
Registry No. $B_2H_7^-$, 27380-11-6.

Dynamic NMR Study of Conjugation in *tert*-Butyl Thioformate¹

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The relative importance of conjugation for first row and second row elements such as oxygen and sulfur has long been of interest.² Evidence for the importance of carbon-sulfur π -bonding has been obtained from molecular orbital studies of substituted carbenium ions,³ in which the sulfur of $^+CH_2SH$ was calculated to be a better π -donor than oxygen in $^+CH_2OH$, and from a dynamic NMR study of thiolacetic acid (**1**),⁴ which showed the rotational barriers



- 1, R = CH₃; R' = H; X = S
- 2, R = H; R' = H; X = S
- 3, R = H; R' = (CH₃)₃C; X = S
- 4, R = H; R' = (CH₃)₃C; X = O

in this compound to be 7.0 and 7.3 kcal/mol. A DNMR study of thioformic acid (**2**) has been claimed;⁵ however, the reported

(1) (a) Presented at the NIH-MBRS Symposium, Albuquerque, NM, April, 1982. (b) This work was supported by the National Institute of Health (Grant No. SO6RR08047).

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