

Computational Evidence for a Metastable Polar Isomer of Beryllium Borohydride

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Although more than 50 years have passed since beryllium borohydride (BeB_2H_8) was first prepared,¹ a complete understanding of its molecular structure has not emerged. Efforts to determine the geometry in early electron diffraction experiments² were compromised by the large number of hydrogen atoms and corresponding difficulties in deconvolving the internuclear radial distribution function with techniques available at that time. Nevertheless, those studies indicated that the B–Be–B framework was linear in BeB_2H_8 . Hydrogen atom positions were impossible to determine unambiguously, but the data were consistent with nonpolar structures having either four (D_{2d} symmetry) or six (D_{3d} symmetry) bridging hydrogens. A flurry of experimental activity in the late 1960s and early 1970s did not succeed in determining the structure, but instead led to considerable confusion and uncertainty. Two separate experiments^{3,4} indicated the presence of a polar BeB_2H_8 isomer with a dipole moment of 2.1 ± 0.5 D. At about the same time, electron diffraction studies produced radial distribution curves qualitatively distinct from those obtained 20 years earlier; some of these were found to be consistent with triangular arrangements of nonhydrogen atoms.⁵ An X-ray study of the solid⁶ was unenlightening, as the crystal is polymeric. Notably, however, the B–Be–B bond angle in the solid state is *ca.* 124° , suggesting that a triangular isomer of this species might be a kinetically viable sublimation product. Perhaps the most important experimental study was carried out by Nibler,⁷ who recorded the infrared and Raman vibrational spectra of both gas-phase and matrix-isolated BeB_2H_8 . This work demonstrated that at least two isomers are present at room temperature while only one persists in the matrix. However, the gas-phase data are not consistent with the presence of a triangular isomer, but rather were ascribed to the D_{2d} and D_{3d} forms. Distortion of the latter along the asymmetric B–Be–B stretching coordinate was not ruled out, and this mechanism was tentatively suggested to account for the apparent polarity.

In an early theoretical study,⁸ Marynick and Lipscomb surveyed no fewer than 11 isomers of BeB_2H_8 . They found that the D_{2d} and D_{3d} forms were considerably more stable than the triangular isomers considered in their survey. Subsequent work¹⁰ on the latter found that none represent local minima on the potential energy surface at the self-consistent field level of theory. In a later study,¹¹ the vibrational spectrum of the D_{2d}

and D_{3d} isomers was predicted using a medium-sized basis set and second-order many-body perturbation theory [MBPT(2)] to treat electron correlation. A compelling agreement was found between the calculated band positions and intensities and those observed in the gas phase. Moreover, the peaks systematically absent in the matrix spectra correspond precisely to those predicted for the D_{2d} structure. Complemented by these results, and further calculations that demonstrate that the D_{3d} form is almost certainly stable with respect to asymmetric B–Be–B distortion,¹¹ Nibler's spectroscopic study⁷ provides strong evidence that the D_{3d} and D_{2d} isomers are thermodynamically competitive, with the former slightly favored. This conclusion has subsequently been verified by a few high-level calculations.¹²

While it now appears that the D_{2d} and D_{3d} isomers of BeB_2H_8 are most abundant, no satisfying explanation for the results of the dipole moment experiments has been provided. To this end, we have reinvestigated the possibility of a stable triangular isomer of this molecule. Before beginning, a brief summary of the aforementioned experiments is warranted. In the first study,³ a species with a dipole moment of 2.1 ± 0.5 D was detected in a dielectric experiment, although nothing about the identity of the compound could be determined. Using the technique of electric deflection, a second experiment⁴ confirmed the presence of a polar species with a molecular weight corresponding to BeB_2H_8 . The refocusing pattern suggests that the direction of the dipole moment is perpendicular to a near-symmetric top axis, clearly consistent with a triangular isomer of BeB_2H_8 . However, the *magnitude* of the dipole moment could not be inferred from this work. Hence, there is strong evidence that a polar isomer of BeB_2H_8 exists, although the oft-cited value of 2.1 ± 0.5 D relies on an assumption that the two experiments probed the same species.

Chemical intuition was used to identify candidate triangular structures of BeB_2H_8 . In our approach, such molecules were viewed as complexes between the BeH cation and B_2H_7^- . Theory suggests that the most stable form of the diborane(7) anion involves two BH_3 units linked by a bridging hydrogen (H_b).¹³ Triangular BeB_2H_8 isomers can then be generated by coordination of the Be–H unit with the terminal hydrogens on each side of B_2H_7^- ; these are differentiated by specific rotational conformations of the BH_3 units in the complex. The three simplest possibilities are idealized C_{2v} structures in which each BH_3 donates either one (**1** in Scheme 1) or two (isomer **2**) hydrogen atoms to the beryllium and the C_s isomer (**3**) in which the beryllium accepts a single bridging hydrogen from one side and two from the other. In our calculations,⁹ which were carried out at the MBPT(2) level with the basis set used in ref 11, each of these structures was optimized by energy minimization and its nature characterized by evaluation of harmonic vibrational frequencies. The results reveal a rather complicated potential energy surface associated with motions that loosely correspond to in-phase (*b* symmetry) and out-of-phase (*a* symmetry) rotations of the BH_3 units about the B– H_b bond axes. Both of the C_{2v} structures **1** and **2** have negative force constants associated with the *a* rotation and therefore necessarily lie above structures with C_2 symmetry; **1** is also unstable with respect to the *b* rotation. Following either of the *a* modes downhill from the respective stationary points leads to the same C_2 structure **4**. However, the force constant for the in-phase *b* rotation in this conformer is negative, which demonstrates that the streambed of the potential surface contains a branch point on the

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Scheme 1

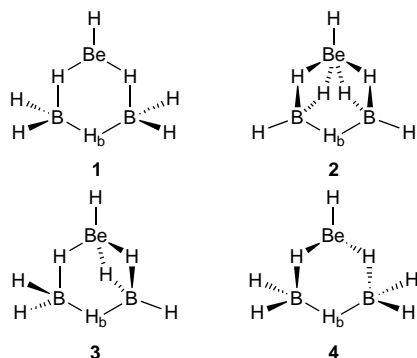


Table 1. Harmonic Vibrational Frequencies and Infrared Intensities for the Metastable C_s Symmetry Isomer of BeB_2H_8^a

mode	symmetry	harmonic frequency (cm^{-1})	infrared intensity (km mol^{-1})
ω_1	a'	2741	42
ω_2	a'	2636	75
ω_3	a'	2368	139
ω_4	a'	2335	127
ω_5	a'	2253	289
ω_6	a'	2183	225
ω_7	a'	1742	14
ω_8	a'	1567	69
ω_9	a'	1450	69
ω_{10}	a'	1184	57
ω_{11}	a'	1123	59
ω_{12}	a'	944	44
ω_{13}	a'	802	33
ω_{14}	a'	716	24
ω_{15}	a'	607	107
ω_{16}	a'	474	3
ω_{17}	a'	446	1
ω_{18}	a''	2740	84
ω_{19}	a''	2387	31
ω_{20}	a''	1384	1
ω_{21}	a''	1133	0
ω_{22}	a''	995	3
ω_{23}	a''	888	0
ω_{24}	a''	658	0
ω_{25}	a''	559	112
ω_{26}	a''	401	1
ω_{27}	a''	27	14

^a All values are obtained at the MBPT(2) level with the basis set described in ref 11.

C_2 symmetry pathway that connects **2** and **4**. Following the b rotation downhill from **4** ultimately leads to **3**, which is a genuine minimum on the potential energy surface. Hence, **4** serves as a transition state which acts to interchange the identity of the two boron atoms. Given the relatively flat nature of the potential surface [**4** lies just 4 kcal mol^{-1} above **3**], triangular BeB_2H_8 is probably highly fluxional. Cartesian coordinates for the metastable structure **3** structure are documented in the supporting information; the corresponding harmonic vibrational frequencies can be found in Table 1. Total electronic and zero-point energies for all BeB_2H_8 species discussed in this work are listed in Table 2.

A significant result is that the potential energy surface of BeB_2H_8 does indeed exhibit a minimum with a triangular arrangement of nonhydrogen atoms. Isomer **3** is the first metastable polar structure to be found, and the potential surface

Table 2. Total Electronic and Zero-Point Vibrational Energies for the BeB_2H_8 Isomers Described in the Text and the $\text{BeBH}_5 + \text{BH}_3$ Dissociation Product^a

species	electronic energy (au)	zero-point energy (kcal mol^{-1})	relative energy ^b (kcal mol^{-1})
D_{3d}	-68.943 918	52.36	0.0
D_{2d}	-68.944 325	53.02	0.9
3	-68.911 977	52.28	20.0
4 ^c	-68.905 303	52.10	24.0
2 ^c	-68.904 168	51.49	24.1
1 ^d	-68.889 996	50.94	32.4
$\text{BeBH}_5 + \text{BH}_3$	-68.879 775	47.78	35.7

^a The lowest energy isomer of BeBH_5 has D_{3d} symmetry, with three equivalent Be-H-B three-center two-electron bonds. All values are calculated at the MBPT(2) level with the basis set of ref 11. ^b Zero-point vibrational contribution included. ^c Structure has one imaginary harmonic frequency. ^d Structure has three imaginary harmonic frequencies.

for hydrogen motions suggests that the presence of another triangular minimum is not likely. While the direction of the dipole moment is consistent with the electric deflection experiment,⁴ its magnitude (1.20 D)¹⁴ is well below that detected in the dielectric study. For reasons stated earlier, however, considerable uncertainty clouds the magnitude of the dipole moment for the mass-selected species studied in ref 4. It should be pointed out that **3** lies about 20 kcal mol^{-1} (see Table 2) above the more stable linear forms, suggesting a negligible mole fraction in the equilibrium vapor at room temperature. Despite extensive effort, however, we have been unable to locate a low-lying transition state that links triangular and linear B-Be-B frameworks. Any such saddle points appear to be well above **3** $\rightarrow \text{BeBH}_5 + \text{BH}_3$ dissociation asymptote, which is predicted to lie at +15.7 kcal mol^{-1} (including zero-point vibrational corrections). Hence, a dissociation/recombination process provides a more likely route for formation of the more stable isomers than does intramolecular rearrangement. Together, these findings suggest that triangular BeB_2H_8 may have an ephemeral existence. Given that the B-Be-B contacts in the crystal are decidedly nonlinear, **3** is a plausible sublimation product. Although it is enticing to speculate that this isomer is indeed the implicated polar structure of BeB_2H_8 , further experimental studies are needed to confirm this hypothesis.

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Supporting Information Available: Table of atomic coordinates (1 page). See any current masthead page for ordering and Internet access instructions.

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(14) This is the value calculated at the MBPT(2) level with the basis set described in ref 11. Additional calculations at higher levels of theory have been carried out and demonstrate that neither basis set nor higher-order correlation effects significantly affect the magnitude of the dipole moment. It is most unlikely that the value presented here differs more than 10% from the exact equilibrium value, meaning that deficiencies in the theoretical treatment cannot account for the apparent discrepancy with the result of ref 3. An estimate of the vibrationally averaged dipole moment is beyond the scope of this work, but a vibrational correction of *ca.* 1.0 D seems unreasonably large.