Inorg. Chem. **1993**, *32,* 487–489

Notes

Application of the ab-Initio/IGLO/NMR Method to the Structure Confirmation of the $[\mu_{5,6}\text{-BHNR}_2\text{-}nido\text{-2,4-C}_2\text{B}_4\text{H}_6]^-$ Ion Intermediate Observed during the Interaction of *closo*-2,4-$C_2B_5H_7$ with $LiNR_2$

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Received August 14, 1992

Introduction

A few years ago it was reported that *closo*-2,4-$C_2B_5H_7$ reacts with $LiNR_2$ (R = CH_3, C_2H_5, $CH(CH_3)_2$) to form, nearly quantitatively, the [*nido*-2,4-$C_2B_4H_7]^-$ ion.[1] An intermediate was reported to build up and then disappear during the course of this reaction. Though it was not possible to isolate this compound, this intermediate was found to exhibit a ^{11}B NMR spectrum that suggests a five-boron compound with C_s symmetry; four different ^{11}B resonances were found, one with area 2.[1] It was speculated[1] that the structure for this intermediate might well be that shown in Figure 1, which represents partial cage opening of the $C_2B_5H_7$ framework.

Recently, the ab-initio/IGLO/NMR method has been applied with some considerable success in the determination of ^{11}B and ^{13}C chemical shifts from MO-optimized structures of known compounds; i.e., the predicted shifts agree exceptionally well with experimentally known NMR chemical shift information.[2-4] The number of successful "experimental vs calculational" correlations that have now been made strongly suggest that structural assignments based on the ab-initio/IGLO/NMR method are quickly approaching a confidence level that rivals modern-day X-ray diffraction determinations of molecular structures. Of course, some caution must be reserved when it is realized that the ab-initio/IGLO/NMR approach most practically involves calculations on a gas-phase, unsolvated, molecule whereas the NMR data are usually gathered from the liquid phase. This does not appear to have posed serious problems, though, for most all of the systems studied to date.[2-4] In this regard it should be mentioned that of those boron compounds studied thus far[3] there has often been an independent structure proof offered for each molecule that was subjected to this type of analysis. Now however, the ab-initio/IGLO/NMR techinque can be considered to provide, in effect, an acceptable independent structure proof method. If the IGLO-calculated values from a suggested structure (optimized by appropriate ab-initio MO methods) match the experimental data reasonably well, it gives considerable credence to such a suggested structure. We recently applied this method to the conjectured structure for an "intermediate" from the *closo*-2,4-$C_2B_5H_7$/$LiNR_2$ reaction mentioned above,[1] and the results are given below.

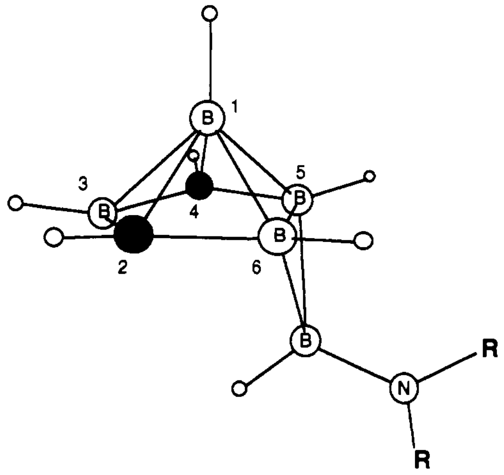

Figure 1. Structure of the $[\mu_{5,6}\text{-BHNR}_2\text{-}nido\text{-2,4-C}_2\text{B}_4\text{H}_6]^-$ ion (R = CH_3, H). Bond distances (in Å) obtained from geometry optimization at the 3-21G level (for the compound where R = CH_3) are as follows: B(1)–C(2) = 1.745, B(1)–B(3) = 1.916, B(1)=B(5) = 1.769, B(5)–B(μ) = 1.921, B(μ)–N = 1.425, N–C = 1.463, B(1)–H = 1.189, B(3)–H = 1.200, B(5)–H = 1.195, B(μ)–H = 1.189.

Experimental Section and Data

Calculational Methods for the Geometry Optimizations and IGLO/NMR Chemical Shift Determinations. Geometry optimization of the the $[\mu_{5,6}\text{-BHNMe}_2\text{-}nido\text{-2,4-C}_2\text{B}_4\text{H}_6]^-$ ion, Figure 1, was approached in the following manner: Initially, we geometry-optimized the parent $[\mu_{5,6}\text{-BH}_2\text{-}nido\text{-2,4-C}_2\text{B}_4\text{H}_6]^-$ ion (with C_s symmetry and with the BH_2

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(1) Abdou, A. J.; Gomez, F.; Abdou, G.; Onak, T. *Inorg. Chem.* **1988**, *27*, 3679.

(2) The IGLO method employed here was designed by: Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919. Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1983**, *105*, 1360–1370. Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1987**, *109*, 1020–1033. Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR, Principles and Progress*; Springer Verlag: Berlin, 1990; Vol. 23, pp 165–262.

(3) The designation "ab-initio/IGLO/NMR" is an Erlangen invention. For examples of the application of IGLO to boron compounds, see: (a) Schleyer, P. v.-R.; Bühl, M.; Fleischer, U.; Koch, W. *Inorg. Chem.* **1990**, *29*, 153. (b) Bühl, M.; Schleyer, P. v.-R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 886. (c) Bühl, M.; Schleyer, P. v.-R. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds. Wiley: New York, 1991; Chapter 4, p 113. (d) Williams, R. E In *Electron Deficient* Boron *and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; Chapter 4, p 91 (see footnote 83). (e) Bühl, M.; Schleyer, P. v. R.; McKee, M. L. *Heteroat. Chem.* **1991**, *2*, 499–506. (f) Bühl, M.; Schleyer, P. v.-R.; Havlas, Z.; Hnyk, D.; Hermanek, S. *Inorg. Chem.* **1991**, *30*, 3107–3111. (g) Bühl, M.; Steinke, T.; Schleyer, P. v.-R.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1160–1161. (h) Bühl, M.; Schleyer, P. v.-R. *J. Am. Chem. Soc.* **1993**, *114*, 477–491. (i) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR, Principles and Progress*; Springer Verlag: Berlin, 1990; Vol. 23, pp 210–212. (j) Köster, R.; Seidel, G.; Wrackmeyer, B.; Blaeser, D.; Boese, R.; Bühl, M.; Schleyer, P. v. R. *Chem. Ber.* **1992**, *125*, 663; *Chem. Ber.* **1991**, *24*, 2715–2724. (k) Kang, S. O.; Bausch, J. W.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1992**, *114*, 6248–6249. (l) Bausch, J. W.; Prakash, G. K. S.; Bühl, M.; Schleyer, P. v.-R.; Williams, R. E. *Inorg. Chem.* **1992**, *31*, 3060–3062. (m) Bausch, J. W.; Prakash, G. K. S.; Williams, R. E. *Inorg. Chem.* **1992**, *31*, 3763–3768. (n) Bühl, M.; Mebel, A. M.; Charkin, O. P.; Schleyer, P. v.-R. *Inorg. Chem.* **1992**, *31*, 3769–3775. (o) Onak, T.; Tseng, J.; Tran, D.; Herrera, S.; Chan, B.; Arias, J.; Diaz, M. *Inorg. Chem.* **1992**, *31*, 3910–3913.

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Table I. ^{11}B NMR Data for the $[\mu_{5,6}$-$BHNR_2$-*nido*-2,4-$C_2B_4H_6]^-$ Ions (R = H, CH_3; δ in ppm)

δ(expt)[a]	assgnt	δ(IGLO/ DZ//3-21G)	δ(expt)[a]	assgnt	δ(IGLO/ DZ//3-21G)
$[\mu_{5,6}$-$BHNMe_2$-*nido*-2,4-$C_2B_4H_6]^-$					
−39.1	B(1)	−41.6	+21	B(3)	+21.7
+7	B(5,6)	+7.6	+49	B(μ)	+49.6
$[\mu_{5,6}$-$BHNH_2$-*nido*-2,4-$C_2B_4H_6]^-$					
N/A	B(1)	−42.3	N/A	B(3)	+21.2
N/A	B(5,6)	+7.3	N/A	B(μ)	+46.5

[a] N/A = not available.

hydrogens in the single plane of symmetry) using the Gaussian code at the STO-3G and, subsequently, the 3-21G levels.[5] Both levels of theory resulted in an optimized structure in which a "frequency" calculation revealed one imaginary (i.e., negative) frequency; therefore this ion species, $[\mu_{5,6}$-BH_2-*nido*-2,4-$C_2B_4H_6]^-$ ion with C_s symmetry, could be considered a "transition state" structure rather than a true minimum on the potential surface. Next, an NH_2 group was substituted, variously, for one the two hydrogens of the bridging BH_2 group of this $[\mu_{5,6}$-BH_2-*nido*-2,4-$C_2B_4H_6]^-$ ion. The placement of the NH_2 group in the endo position (relative to the open five-atom face of the cage) did not give rise to a vibrationally stable structure whereas placement of the NH_2 group in the exo position did give rise to a vibrationally stable molecule ion ($[\mu_{5,6}$-$BHNH_2$-*nido*-2,4-$C_2B_4H_6]^-$; HF = −257.431 12 au at the 3-21G geometry optimized level; HF(MP2/6-31G*//3-21G) = −259.747 30 au) but only when the NH_2 hydrogens were placed in the C_s plane (defined by B3–B1–H1; see Figure 1). Methyl groups were then substituted for the two NH_2 hydrogens, and the structure was submitted to a full 3-21G optimization procedure. A vibrationally stable species was obtained, Figure 1 (HF = −355.051 50 au at the 3-21G geometry optimization level).

The Gaussian calculations were carried out on, variously, Alliant FX/2800, Multiflow-Trace, and Elxsi minisupercomputers. The structures for the various molecules were verified by constructing ball and stick models of each species directly from the optimized coordinates using the the Molecular Editor application on a Mac-IIci computer. The optimized coordinate output for each molecule was used as the input coordinate set for the IGLO calculations at the the DZ level.[2-4] The consequent ^{11}B chemical shifts, determined from IGLO calculations, were referenced to B_2H_6 as the primary reference, and these δ values were then converted to the standard $F_3B{\cdot}OEt_2$ scale using the experimental value of +16.6 ppm for $\delta(B_2H_6)$.[6]

Results and Discussion

The IGLO analyses of both the $[\mu_{5,6}$-$BHNH_2$-*nido*-2,4-$C_2B_4H_6]^-$ and $[\mu_{5,6}$-$BHNMe_2$-*nido*-2,4-$C_2B_4H_6]^-$ ions were performed at the DZ level on the 3-21G optimized geometries. The (IGLO) predicted ^{11}B chemical shifts are given in Table I, and in the case of $[\mu_{5,6}$-$BHNMe_2$-*nido*-2,4-$C_2B_4H_6]^-$ ion, they are given alongside the experimentally observed chemical shift data obtained for the intermediate[1] observed from the reaction of *closo*-2,4-$C_2B_5H_7$ with $LiNMe_2$. (It may be significant to note that the presence of other alkyl groups on the nitrogen, such as ethyl or isopropyl, does not appreciably affect the experimentally observed chemical shifts of the intermediate species.)[7] Considering that the calculational work is carried out on an unsolvated species and the experimentally obtained data are gathered from solution spectra, and the correspondence is excellent. Schleyer and others have found a similar agreement between experimental and calculated ^{13}C NMR chemical shifts of carbocations where solvation effects mught initially be expected to pose problems.[4]

The 3.1 ppm (IGLO calculated; see Table I) upfield shift for $^{11}B(\mu)$ upon substituting H for CH_3 (for substituent R in $[\mu_{5,6}$-$BHNR_2$-*nido*-2,4-$C_2B_4H_6]^-$; Figure 1) of the carborane anion is more reminiscent of the analogous $^{13}C(1)$ shift of a phenyl group attached to a trivalent nitrogen (ca. 2 ppm upfield shift upon substituting H for CH_3 for R of $R_2NC_6H_5$)[8-10] than that found for $^{13}C(1)$ of an aliphatic group attached to a trivalent nitrogen (ca. 12–19 ppm upfield shift upon substituting H for CH_3 for R of R_2NR', with R′ = alkyl).[11] This may be significant when one combines this correlation with that observed for the amine adduct of $C_2B_6H_8$.[3o] In that instance a 14.4 upfield shift is found upon comparing the IGLO-calculated $^{11}B(4)$ shift for

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(6) Onak, T.; Landesman, H. L.; Williams, R. E.; Shapiro, I. *J. Phys. Chem.* **1959**, *21*, 51.

(7) Data for $[\mu_{5,6}$-$BHNR_2$-*nido*-2,4-$C_2B_4H_6]^-$: δ(B1) = −39.1, δ(B5,6) = +6.7, δ(B3) = +21.0, δ(Bμ) = +48.5 for R = C_2H_5; δ(B1) = −39.5, δ(B5,6) = +7, δ(B3) = +21, δ(Bμ) = +47 for R = $CH(CH_3)_2$.[1]

(8) The ^{13}C chemical shift of the carbon, C(1) attached to the nitrogen of aniline is 2.0 ppm higher field than that of the corresponding carbon of *N,N′*-dimethylaniline (p 257 of ref 9); the C(1) chemical shift of the phenyl group of trimethylphenylammonium ion is 0.7 ppm higher field than that of aniline (p 257 of ref 9); the ^{13}C chemical shift of the C(1) position of anilinium ion is 17.6 ppm (in CCl_4 solvent) to higher field than C(1) of aniline;[10] therefore, the $^{13}C(1)$ chemical shift of anilinium ion is 16.9 ppm upfield of that of the trimethylphenylammonium ion.

(9) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd ed.; VCH: Germany, 1987.

(10) Nelson, G. L.; Levy, G. C.; Cargioli, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 3089–3094.

(11) See pp 237 and 315 of ref 9.

(12) Bullen, G. J.; Clark, N. H. *J. Chem. Soc. A* **1970**, 992–996.

(13) The remarks of one of the reviewers include the following: "In the present instance, 3-21G ab initio geometries are found to be adequate for good IGLO comparisons with experiment. However, this is not generally the case and a cautionary note should be included." We disagree with the portion of the statement "... not generally the case..", when applied to ^{11}B NMR comparisons within carborane clusters. In the published literature[3] (and also studies presently in progress here and in other laboratories), calculations performed on geometries optimized at the 3-21G level have, in our opinion, given splendid ^{11}B correlations for carboranes. The ab-initio/IGLO/NMR calculations performed at the DZ//3-21G level (a) seem to be excellent in predicting the correct chemical shift order within each compound and (b) will predict for most all carboranes the actual δ value for each boron within a couple percent of the entire range of experienced chemical shifts (note: boron chemical shifts of all known carboranes fall within a fairly wide range of ca. 100 ppm). Nevertheless we concur with the reviewer in that ab-initio/IGLO/NMR calculations should normally be carried out at the highest level that is feasible, preferably BASIS-II//MP2/6-31G*, but perhaps no lower than DZ//3-21G for molecules where the size of the compound and the degree of calculational resources dictate lower calculational levels. However, even use of STO-3G-optimized geometries almost always results in the same boron chemical shift trends (via IGLO analysis) as are experimentally observed for different borons within the same molecule. To our knowledge no definitive MO/NMR calculational study has dealt with the problem of obtaining theoretical ^{11}B δ values (for clusters) properly averaged over vibrational and rotational contributions or dealt with changes in ^{11}B δ values as a function of temperature and bulk interaction effects. When such studies are carried out, it would not be surprising to find that the very small differences between geometry-optimized 3-21G and MP2/6-31G* (ground-state) structures may, in many instances, be overshadowed by other aspects of the overall chemical shielding determination. Additionally, there is the problem of accurate chemical shift determinations by experimental means. Not infrequently, boron resonances are broad, and the accuracy (or inaccuracy) with which the resonance center is determined may be on the order of ±1, or more, ppm. Furthermore, internal referencing of ^{11}B NMR shifts to a common reference species is rare. The agreement of experimentally obtained data with the IGLO-calculated shifts in these cases cannot be expected to be better than the error involved in obtaining the experimental data. Then there is the aggravating problem of ascertaining the chemical shift values of certain secondary reference points. For the IGLO shifts the reference is (gaseous) B_2H_6 with an ostensible δ value of 16.6; however, this experimentally determined shift was reported over three decades ago when NMR instrumentation did not often allow for very accurate assessments of chemical shifts, especially for weak resonances obtained from gas-phase spectra. Added to this is an uncertainty concerning the B_2H_6 geometry (experimental vs optimized geometries at various specific calculational levels) to be employed for the IGLO calculations. The chemical shift reference-point problem, of course, would only affect the intercept, and not the slope, of any IGLO/experimental comparison of shielding values. The intercept problem aside, when other factors (vide supra) are considered it is expected that the most reliable correlations will be encountered upon comparing various boron chemical shifts (IGLO vs experimental) within the same molecule, for one could then anticipate the cancellation of many, or most all, experimental and calculational errors.

4-H_3N-1,3-$C_2B_6H_8$ to that actually observed for the $^{11}B(4)$ in 4-Me_3N-1,3-$C_2B_6H_8$, both containing quaternary nitrogens;[3o] the comparison ^{13}C data are to be found in the $^{13}C(1)$ chemical shift of anilinium (and its *N,N′,N″*-trimethyl derivative) ion in which the parent compound shows a $^{13}C(1)$ chemical shift value that is 16.9 ppm upfield of that of trimethylphenylammonium ion;[8–10] in contrast, there is only a 3.5 ppm upfield shift when proceeding to $^{13}C(1)$ of the pentylammonium ion from the $^{13}C(1)$ chemical shift of the corresponding N,N′,N″-trialkylated derivative of that compound.[11] This indicates that the polyboranyl groups in both instances, the [$\mu_{5,6}$-$BHNR_2$-*nido*-2,4-$C_2B_4H_6$]$^-$ ion and the 4-Me_3N-1,3-$C_2B_6H_8$ adduct, are behaving in a fashion that parallels "aromatic" rather than "aliphatic" carbon systems.

The bond distances found for the 3-21G-optimized structures of both ion molecules [$\mu_{5,6}$-$BHNH_2$-*nido*-2,4-$C_2B_4H_6$]$^-$ and [$\mu_{5,6}$-$BHNMe_2$-*nido*-2,4-$C_2B_4H_6$]$^-$ (Figure 1) are very similar. The calculated BN bond distances of 1.42–1.43 Å in each of the two ions are on the order of that found for the only simple comparison compound we could find, i.e., Me_2BNMe_2,[12] in which a nitrogen-boron bond distance had been reported.

In conclusion, it seems highly likely that the structure previously proposed for an important intermediate in the reaction of *closo*-2,4-$C_2B_5H_7$ with $LiNR_2$, and observed by the use of ^{11}B NMR chemical shift information, is correct. This conclusion is reached by the excellent correlational results obtained from the application of the ab-initio/IGLO/NMR technique to the problem.[13]

Acknowledgment. The authors wish to thank the NSF, Grant CHE-8922339, for support of this project. M.D., J.A., and S.H. thank the MBRS-NIH program for partial support; D.B. and J.A. also thank the NSF-RIMI program for partial support. We also thank California State University, Sacramento, CA, for access to the Multiflow Trace (NSF Grant CHE-8822716) minisupercomputer facilities and San Diego State University for access to the Elxsi minisupercomputer. We also wish to thank M. Schindler for permission to use the IGLO program designed by W. Kutzelnigg and M. Schindler, and we thank R. T. Keys for helpful discussions.