CORRELATION OF EXPERIMENTAL STRUCTURAL AND ^{11}B NMR DATA TO CALCULATIONAL RESULTS FOR THE $[2\text{-}CH_3CN\text{-}B_{10}H_9]^-$ ION

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Abstract

The $[2\text{-}CH_3CN\text{-}B_{10}H_9]^-$ ion, recently reported by Shore, Hawthorne, et al, is analyzed by ab-initio geometry optimization, IGLO/NMR and FPT-INDO methods; and the ion, with its unique B-N bond, is compared to some of our B-N containing substituted polyborane systems.

Introduction

Recently, the synthesis of an acetonitrile derivative of $[B_{10}H_{10}]^{2-}$ ion was reported(1) along with X-ray derived structural parameters as well as with ^{11}B NMR data and assignments. This compound contains an N-B bond along an equatorial belt of the cluster. Our interest in this unique compound reported by Hawthorne, Shore, et al, stems from our studies on other boron-bonded nitrogen derivatives of polyboranes (e.g. *B*-$Me_3N\text{-}C_2B_4H_6$(2), *B*-$Me_3N\text{-}C_2B_5H_6Cl$(3); *B*-$Me_3N\text{-}C_2B_6H_8$(4); *B*-$Me_3N\text{-}C_2B_7H_9$(5); and $[\mu_{5,6}\text{-}BHNR_2\text{-}nido\text{-}2,4\text{-}C_2B_4H_6]^-$ Ion(6)). For comparison with these carborane N-B systems we examined the geometry optimization of the $[2\text{-}CH_3CN\text{-}B_{10}H_9]^-$ ion and the application of IGLO(7-9) and FPT-INDO(10) calculational methods. This was performed in order to compare theoretically derived structural and NMR parameters of the ion with those experimentally available.

Calculational Methods for the Geometry Optimizations, and for IGLO/NMR Chemical Shift and FPT-INDO/NMR Coupling Constant Determinations

An energy optimized structure for the $[2\text{-}CH_3CN\text{-}B_{10}H_9]^-$ ion was carried out using the ab initio Gaussian-90 and Gaussian-92 codes(11) with split valence basis sets at the HF/3-21G level and with polarization functions at the HF/6-31G* level of theory. Each full-geometry optimization ultimately resulted in a stable structure. The total energy is -381.90102 A.U. for the 3-21G fully optimized structure and -384.05316 A.U. for the 6-31G* fully optimized structure. Depicted in Figure 1 is the molecule ion which was optimized at the HF/6-31G* level (note: the same basic structure was also obtained at the HF/3-21G level of geometry optimization) and in Table 1 are listed the bond distances obtained at the higher level of theory. The energy optimized structures were used to calculate the chemical shieldings using the IGLO(7) code, and to compute the coupling constants using the FPT-INDO method.(10) All IGLO calculations were performed with a double-ζ set (DZ)(12) in the contractions (21) for H, and (4111/21) for first row elements. All IGLO calculated ^{11}B shielding values σ were referenced to B_2H_6 as the primary reference point. The resulting chemical shifts δ in Table 2 were converted to the standard $F_3B{\cdot}OEt_2$ scale using the experimental value of +16.6 ppm for $\delta(B_2H_6)$;(13) thus, $\delta(^{11}B \text{ of cpd}) = \sigma(^{11}B \text{ of } B_2H_6) - \sigma(^{11}B \text{ of cpd}) + 16.6$ ppm. The shielding for B_2H_6 [$\sigma(^{11}B \text{ of } B_2H_6)$] is 114.9 ppm at the double-ζ level which then implies that the shielding for $F_3B{\cdot}OEt_2$ is 131.5 ppm. All calculations were carried out, variously, on Multiflow-Trace, and SUN 4/280, and SUN SPARC station Model 10 computers.

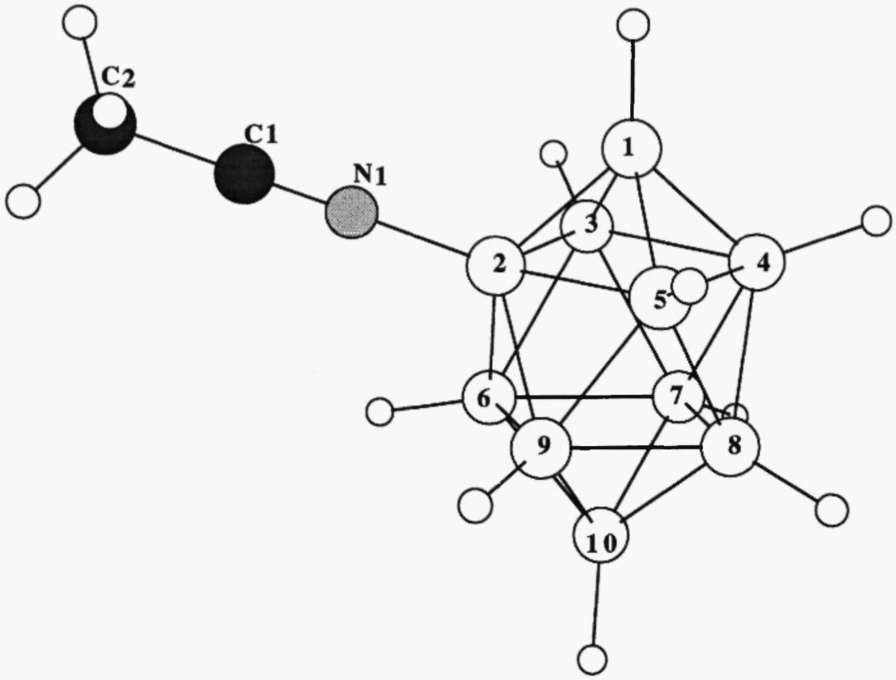

Figure 1. The 6-31G* fully optimized structure of the [2-CH_3CN-$B_{10}H_9$]$^-$ ion; this is in excellent agreement with the experimental structure previously published.(1); see Table 1 and Figure 2.

Discussion

Geometry optimizations of the [$CH_3CNB_{10}H_9$]$^-$ ion at each of two levels of theory, 3-21G and 6-31G*, provide a vibrationally stable structure which, in both cases, results in bond distances that compare very favorably to each other (Figure 3) and to those(1) obtained from X-ray structural data (Table 1 and Figure 2). The greatest deviation from the linear correlation involves various B-H bond distances, but that can be readily rationalized by realizing the difficulty in locating the hydrogen positions relative to the heavier atoms utilizing the X-ray structure method. The full geometry optimizations at both examined levels of theory indicated, as was also experimentally found, that the CCNB sequence of bonds is well within 1° of linearity.

Table 1. Bond Distance Data for the [2-CH_3CN-$B_{10}H_9$]$^-$ Ion, in (Å)

Bond	Experimental[1]	3-21G	6-31G*
B1-H1	1.110	1.189	1.195
B1-B2	1.670	1.702	1.685
B1-B3	1.684	1.732	1.717
B1-B4	1.680	1.709	1.695
B1-B5	1.694	1.732	1.717
B2-N1	1.515	1.534	1.534
B2-B3	1.797	1.838	1.813
B2-B5	1.806	1.838	1.813
B2-B6	1.780	1.815	1.804
B2-B9	1.794	1.815	1.804
B3-H3	1.110	1.191	1.196
B3-B4	1.826	1.870	1.847
B3-B6	1.826	1.866	1.859
B3-B7	1.807	1.835	1.827
B4-H4	1.070	1.191	1.196
B4-B5	1.817	1.870	1.847
B4-B7	1.816	1.853	1.844
B4-B8	1.804	1.853	1.844
B5-H5	1.120	1.191	1.196
B5-B8	1.804	1.835	1.827
B5-B9	1.830	1.866	1.859
B6-H6	1.200	1.195	1.200
B6-B7	1.820	1.862	1.841
B6-B9	1.831	1.889	1.867
B6-B10	1.686	1.713	1.698
B7-H7	1.170	1.191	1.197
B7-B8	1.831	1.880	1.855
B7-B10	1.687	1.724	1.708
B8-H8	1.100	1.191	1.197
B8-B9	1.824	1.862	1.841
B8-B10	1.688	1.723	1.708
B9-H9	1.170	1.194	1.200
B9-B10	1.695	1.713	1.695
B10-H10	1.060	1.188	1.194
N1-C1	1.129	1.131	1.125
C1-C2	1.440	1.457	1.464
C2-H2A	1.000	1.083	1.082
C2-H2B	1.000	1.083	1.082
C2-H2C	1.000	1.083	1.082

Table 2. NMR Calculational and Experimental Data for the [2-CH_3CN-$B_{10}H_9$]$^-$ Ion

Assignment	^{11}B Chemical shifts (ppm)			J (^{11}B-H), Hz	
	IGLO/DZ on 3-21G Geometry	IGLO/DZ on 6-31G* Geometry	Exptl[1]	FPT-INDO; from 6-31G* geometry	Experimental[a]
B1	-5.9	-6.7	-1.5	137	163.7
B2	-22.9	-23.6	-19.9	-	Not reported
B4	-21.3	-23.0	-26.6	118	143.3
B10	-1.7	-2.9	1.2	133	143.3
B3,5	-24.1	-25.2	-27.8	122	135.9
B7,8	-24.4	-25.6	-25.2	117	Not reported
B6,9	-24.3	-25.3	-27.8	118	Not reported

[a] Experimental J data[1] is most likely derived from a 1st order interpretation of the obtained spectrum.

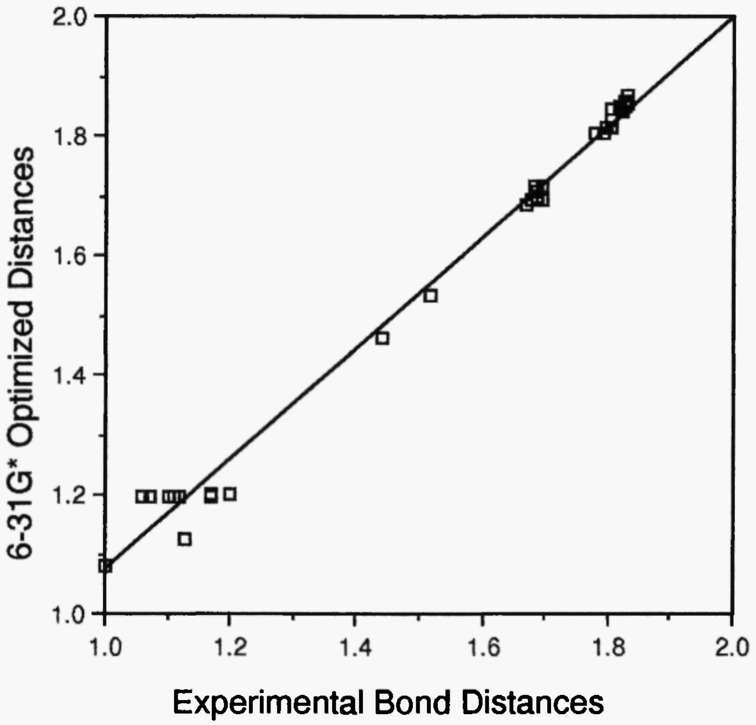

Figure 2. Experimental bond distances(1) vs 6-31G* optimized distances; y(6-31G*) = 0.928x(exp) + 0.148; r^2 = 0.993.

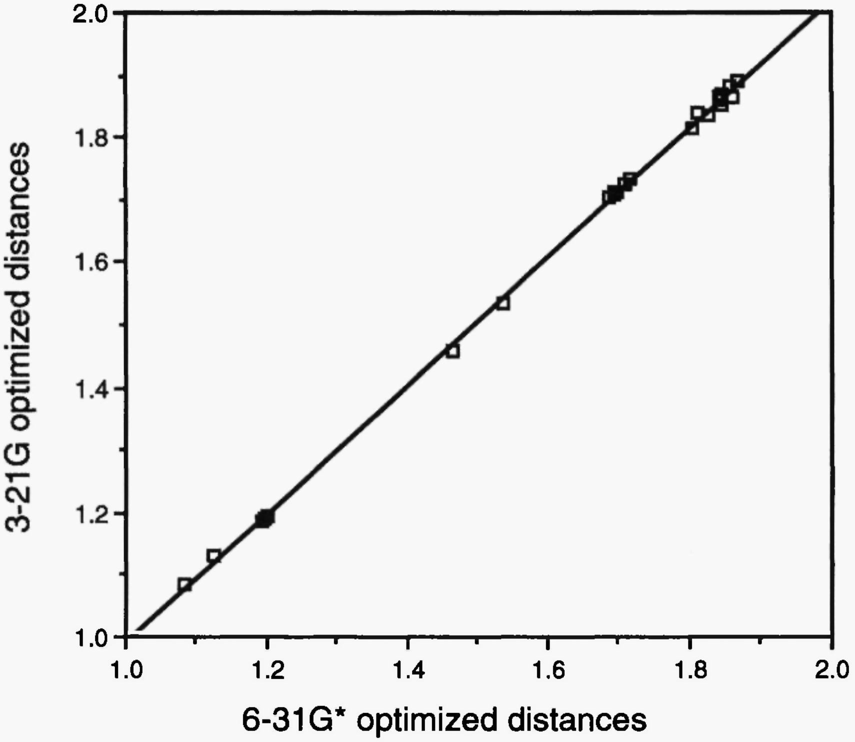

Figure 3. Geometry optimized distances for $[CH_3CNB_{10}H_9]^-$ ion, 3-21G vs 6-31G*; y(3-21G) = 1.03x(6-31G*) - 0.0373; $r^2 = 0.9999$

The IGLO NMR chemical shifts (Table 2) compare very favorably with the assignments previously derived from a ^{11}B-^{11}B COSY experiment.(1) A linear relationship (correlation coefficient $r^2 = 0.96$) obtained from a comparison of the IGLO calculated (DZ//6-31G*) boron-11 chemical shifts with the experimentally observed chemical shifts is very good.

The FPT-INDO method has been used to predict coupling constants, and although the absolute calculated values are not expected to match perfectly with experimentally determined coupling constants, it is expected that similar trends are seen in the comparison of both experimental and calculational results. Indeed, for those three B-H couplings reported in the literature, the trend $J(B_1H) > J(B_{10}H) > J(B_{3,5}H)$ is mimicked by the values calculated from FPT-INDO calculations on the 6-31G* fully optimized structure. The fact that the experimental coupling values are all somewhat larger than the calculated values can (partially) be attributed to the difficulty in carrying out an appropriate second-order analysis of the experimental spectrum. (For example, we found that a second order analysis of the H-^{13}C spectrum of closo-1,5-$C_2B_3H_5$ reveals a $^1J(CH)$ that is about 15% lower than a first order analysis of the spectrum)(14). The ^{11}B-^{11}B COSY spectrum(1) shows that the B(2)-B(3,5) cross peak is the weakest of the 'adjacent-boron' cross peaks; and it is interesting to note that the FPT-INDO calculations on the 6-31G* geometry predicts that the $^{11}B(2)$-$^{11}B(3,5)$ coupling should be significantly weaker (5.1 Hz) than many of the other 'adjacent boron' cross peaks (i.e., 9.5 Hz for $^{11}B(10)$-$^{11}B(6,9)$; 8.2 Hz for $^{11}B(1)$-$^{11}B(3,5)$.

The above correlations, along with those previously obtained from several N-B bonded amine-carboranes,[4-6] show that the pertinent calculational results are reasonably reliable for these nitrogen containing polyborane systems. It is interesting to note that the B-N bond distance in the $[CH_3CNB_{10}H_9]^-$ ion (1.52 Å experimentally[1], 1.53 Å at both 3-21G and 6-31G* levels of geometry optimization) is intermediate to that of 4-H_3N-1,3-$C_2B_6H_8$ (1.63 Å at 3-21G level, 1.62 Å at 6-31G* level of theory)(8o,14) and that of $[\mu_{5,6}$-$BHNR_2$-*nido*-2,4-$C_2B_4H_6]^-$ ion(6,14) (1.42 Å at the 3-21G level for R = H; 1.43 Å at the 6-31G* level of theory for R = CH_3). This is not unreasonable in that the latter compound would be expected to have some degree of B=N double bond character; and the 4-H_3N-1,3-$C_2B_6H_8$ adduct should involve an sp^3 hybridized nitrogen whereas the $[CH_3CNB_{10}H_9]^-$ ion involves a B-N bond with an sp hybridized nitrogen.(15)

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