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Electron Paramagnetic Resonance Study of the Reaction of Ground-State Al Atoms with NH_3 in a Rotating Cryostat[†]

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Abstract: An electron paramagnetic resonance spectroscopic study of the reaction of ground-state Al atoms with NH_3 in adamantane at 77 K on a rotating cryostat has demonstrated the formation of three mononuclear Al–NH_3 complexes, $Al(NH_3)_4$ (**A**), $HAlNH_2$ (**B**), and $Al(NH_3)_2$ (**C**). These species have the following magnetic parameters: $a_{Al} = 786.3 \pm 0.22$ MHz, $a_N = 23 \pm 0.08$ MHz, and $g = 1.9997 \pm 0.0001$ for $Al(NH_3)_4$, $a_{Al} = 922.5 \pm 0.41$ MHz, $a_H = 228.7 \pm 2.00$ MHz, $a_N = 27 \pm 2.0$ MHz, $a_H(1) = 27 \pm 2.0$ MHz, and $g = 2.0003 \pm 0.0002$ for $HAlNH_2$, and $a_{\parallel}(Al) = 131.5$ MHz, $a_{\perp}(Al) =$ ca. 20 MHz, and $g_{\parallel} = g_{\perp} = 1.999$ for $Al(NH_3)_2$. HAlOH (**D**) is also formed in this system from adventitious H_2O and has the parameters $a_{Al} = 911.3 \pm 1.06$ MHz, $a_H = 286.4 \pm 3.7$ MHz, and $g = 1.9998 \pm 0.0004$.

Introduction

Spectroscopic studies of the reaction of metal atoms with ammonia have been largely confined to the reaction of ground-state group 1 metal atoms (^2S) with a large excess of NH_3 that give deep blue or blue-violet deposits from solvated or trapped electrons.[1-3] However, when ND_3 was condensed onto ^7Li, crystalline $^7Li(ND_3)_3{\cdot}ND_3$ was formed and found to have a slightly distorted pyramidal structure by X-ray crystallography.[4] In addition, matrix isolation electron paramagnetic resonance (EPR) spectroscopy has demonstrated that Li atoms and NH_3 in argon at ca. 15 K give the molecular complex $LiNH_3$.[5]

Ground-state Mg and Ca atoms (^1S) produce highly colored deposits in NH_3 from solvated electrons[3] while electronically excited Mg atoms (^3P) react with NH_3 to give $Mg\dot{N}H_2$ and $H^{\bullet}$ at low temperatures and $Mg(NH_2)_2$ and $H^{\bullet}$ at higher temperatures in the presence of excess NH_3.

It has been reported[2,3] that reaction of Al atoms with excess NH_3 results in the formation of aluminium amide (**1**) and hydrogen. Ammonia is lost when **1** is warmed yielding the polymeric nitride (**2**).

$$Al + 3NH_3 \rightarrow \underset{\mathbf{1}}{Al(NH_2)_3} + 1.5H_2$$

$$Al(NH_2)_3 \rightarrow \underset{\mathbf{2}}{AlN} + 2NH_3$$

The failure of the initial material to convert but-2-yne to but-2-ene suggested that solvated electrons were not present despite the intense black color of the deposit.[2,3]

As part of an electron paramagnetic spectroscopic (EPR) study of the reactions of ground-state Al atoms with organic[6-13] and inorganic[14,15] substrates in hydrocarbon matrices at 77 K, we have investigated the reaction of these atoms with NH_3 and the results are reported here.

Experimental Section

^{27}Al atoms (^2P, $I = {}^5/_2$) were produced from the metal (~25 mg of aluminum wire, Alpha) in a resistively heated tungsten-coil furnace (No. 12070 Ernest F. Fullam, Schenectady, NY) and were deposited at a rate of ~0.06 g/h onto a band of adamantane (Aldrich) at 77 K that had previously been deposited onto the drum of a rotating cryostat.[16,17] The Al atoms were bombarded with NH_3 and the products were covered with a fresh layer of adamantane (the ratio of adamantane to NH_3 was ~ 14:1). At the end of the run (ca. 10 min) the resulting deposit was transferred under high vacuum ($<10^{-5}$ Torr) from the drum still at 77 K to an EPR tube. The deposit was next examined by EPR spectroscopy (Bruker ESP 300). Al atoms were also reacted with $^{15}NH_3$ and ND_3, both of which were obtained from MSD, Montreal.

Magnetic parameters were calculated from exact solutions of the Breit-Rabi equation by using a computer program written by Dr. K. F. Preston (NRCC). Powder spectra were simulated by using a program provided by Professor R. L. Belford (University of Illinois, Urbana).

Results and Discussion

The EPR spectrum of the reddish-brown deposit from reaction of ^{27}Al ($I = {}^5/_2$) atoms with NH_3 in adamantane at 77 K is shown in Figure 1. It consists of at least four overlapping spectra labeled A, B, C, and D with the amplitude of C much greater than the other three spectra. The analysis of these four spectra will be considered separately.

Spectrum A: The sextet of broad lines centered at $g = 1.9997 \pm 0.0001$ (labeled A) has a large hyperfine interaction of 786.3 ± 0.22 MHz from one Al nucleus. The $M_I = {}^1/_2$ line of this spectrum resolved, on warming the sample to 123 K, to give 9 lines with a spacing of 23 ± 0.08 MHz (Figure 2a). The relative intensities of these lines indicate four equivalent ^{14}N ($I = 1$) nuclei and therefore four ligands each containing one N nucleus, i.e., the carrier of the spectrum was most probably $Al(NH_3)_4$. There was no evidence for a proton hyperfine interaction in this spectrum because Al and ND_3 gave the same nine-lined $M_I = {}^1/_2$ transition

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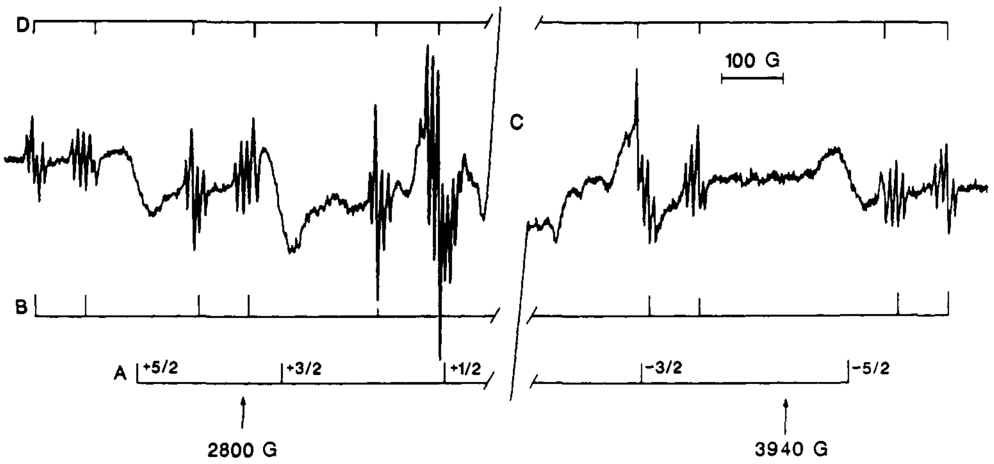

Figure 1. EPR spectrum given by Al atoms and NH_3 in adamantane at 77 K (ν = 9448.7 MHz and power = 50 mW). Note that C represents the central features which are off scale at the receiver gain necessary to record A, B, and D.

(Figure 2b) as was observed for Al and NH_3. Spectrum A from Al and $^{15}NH_3$ (^{15}N has $I = {}^1/_2$) was consistent with this assignment since the $M_I = {}^1/_2$ transition resolved to give a pentet with a spacing of 31 MHz (Figure 2c).

Dividing the observed Al hfi of species A by the one-electron atomic parameter for the 3s orbital of Al (A = 3911 MHz)[18] gives an unpaired 3s spin population, ρ_{3s}, equal to 0.20. The remaining unpaired spin on Al may reside in a 3p orbital, but we were unable to determine its contribution because the spectrum was almost isotropic. The small ^{14}N hfi of 23 MHz is isotopic and probably arises by spin polarization of the ^{14}N 2s electrons. Dividing this N hfi by A = 1811 MHz for ^{14}N gives ρ_{2s} = 0.013.

The $Al(NH_3)_4$ species is isoelectronic with ClF_4, a radical first studied by EPR spectroscopy by Morton and Preston.[19] The authors concluded that ClF_4 has a square-planar structure (D_{4h}) because the F atoms are equivalent and the ^{35}Cl hyperfine interaction indicates the SOMO possesses considerable s character (17%). The D_{4h} configuration with a $^2A_{1g}$ ground state was later supported by an unrestricted SCF MO calculation.[20]

Most of the paramagnetic Al(0) species that we have studied thus far have 7 valence electrons. Thus $Al(NH_3)_4$ has 11 electrons in its valence shell and is an example of a hypervalent molecule.

We can obtain a bonding model for $Al(NH_3)_4$ by using the Lewis–Langmuir[21,22] octet theory and the concept of valence shell orbital hybridization.[23] Since $Al(NH_3)_4$ has 4 pairs of electrons donated by the ligands, a lone pair and an unpaired electron, six orbitals are required which suggests that Al undergoes sp^3d^2 hybridization. It is interesting that the s contribution is 17% which is close to our empirical value of 20%.

The involvement of d orbitals to explain bonding in hypervalent molecules has been criticized on the basis of the large promotional energies involved.[24] Alternatively we could invoke the three-center-bond model in which four NH_3 ligands donate their $3a_1$ electrons into the lobes of the empty p_x and p_y Al orbitals. Hybridization of the remaining 3s and $3p_z$ orbitals provides two sp hydrids to accommodate the lone pair and the odd electron. This model predicts 50% s character which is considerably larger than that calculated from the Al hfi.

A molecular orbital diagram (Figure 3) can be assembled by using the valence 3s and 3p Al orbitals and the bonding orbitals of NH_3. The atomic orbitals of Al transform to a_{1g}, e_u, and a_{2u} while the ligand orbitals are divided into three sets with a_{1g}, e_u, and b_{1g} symmetry. The Al and NH_3 orbitals with a_{1g} and e_u symmetry interact to form bonding and antibonding orbitals. The ligand b_{1g} and the Al a_{2u} orbitals find no orbitals of proper symmetry with which to interact and remain nonbonding. In filling the orbitals three pairs of electrons are located in bonding orbitals, two in nonbonding orbitals and the odd electron in an antibonding $2a_{1g}$ orbital. It is important to note that in this MO description the SOMO also has considerable s character.

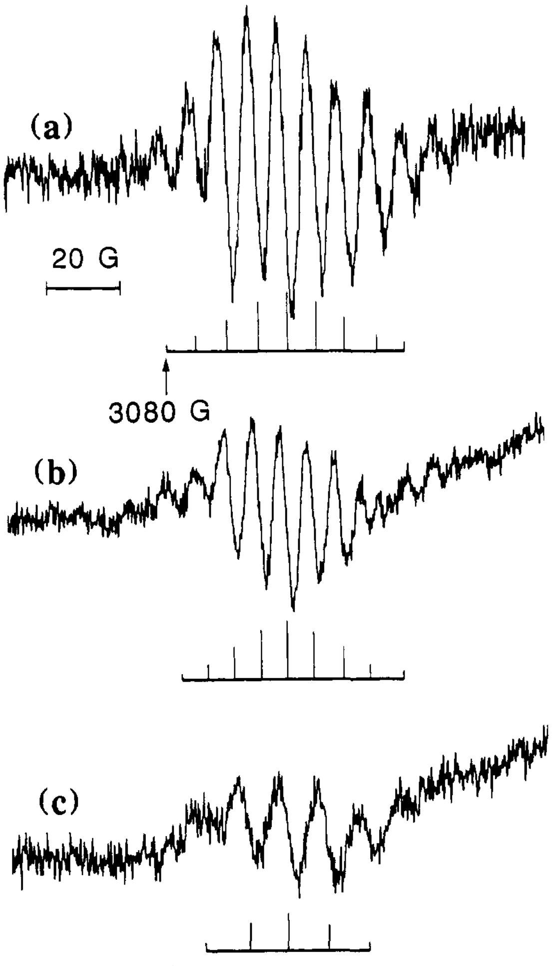

Figure 2. The $M_I = {}^1/_2$ transition of $Al(NH_3)_4$ (A) at 123 K (a), $Al(ND_3)_4$ at 77 K (b), and $Al(^{15}NH_3)_4$ at 77 K (c) in adamantane.

Spectrum B: An almost isotropic sextet of doublets of what seemed to be quartets, labeled B in Figure 1, was also apparent. Analysis of this spectrum gave an Al hfi of 922.5 ± 0.41 MHz and a doublet spacing of 228.7 ± 2.0 MHz, centered at g = 2.0003 ± 0.0002. The doublet spacing was similar to that of other species

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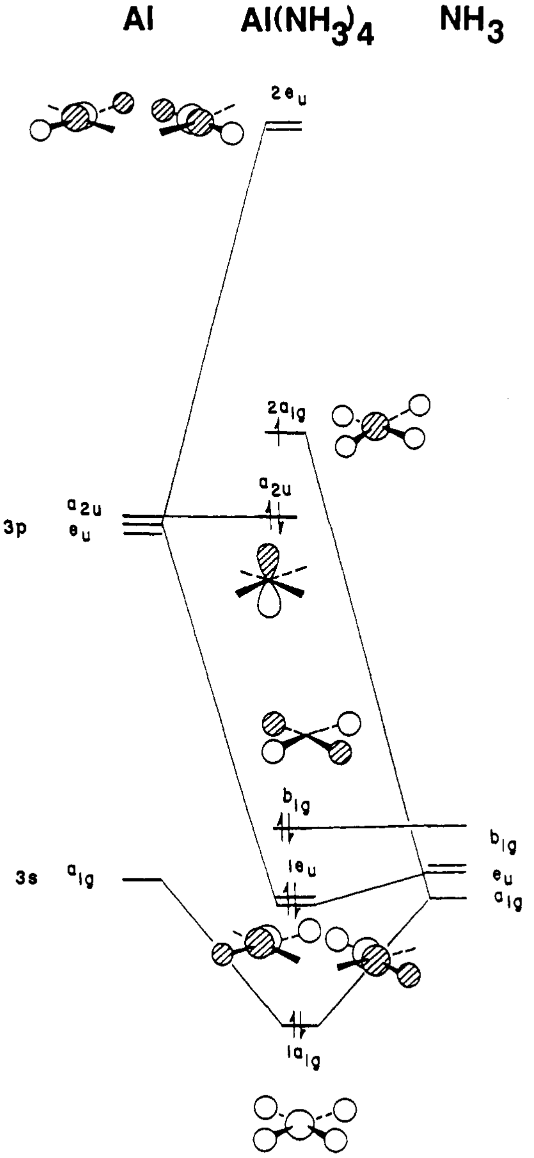
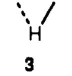


Figure 3. Molecular orbital diagram of $Al(NH_3)_4$ in a square-planar (D_{4h}) configuration. Only s and p orbitals are considered on Al.

with an Al-H bond, e.g., HAlOH[8,25] ($a_{\mathrm{H}} = 282$ MHz) and C_3H_5AlH[9] ($a_{\mathrm{H}} = 161$ MHz), and was assigned to a unique hydrogen nucleus directly bonded to Al. The Al hfi of B was nearly identical to the Al isotropic hyperfine interaction of the divalent neutral aluminum radical HAlOH ($\langle a_{\mathrm{Al}} \rangle = 921$ MHz).[25] We therefore conclude that the carrier of this spectrum is the isoelectronic species $HAlNH_2$ produced by insertion of the Al atom into an HN bond of NH_3. We believe that the quartet pattern of superhyperfine interactions arises through coupling to one N and *one* H nucleus with $a_{\mathrm{N}} = a_{\mathrm{H}} = 27$ MHz and that the structure of $HAlNH_2$ has a bridging H as shown in **3**. A simulation of one of the doublets of quartets by using $a_{\mathrm{H}} = 228.7$ MHz, $a_{\mathrm{N}} = a_{\mathrm{H}} = 27$ MHz gave an exact fit with the experimental spectrum. The absence of a resolved coupling to the second amino hydrogen is not unexpected as the hydroxyl H of HAlOH is also not resolved. This assignment appears to be confirmed by the observation that Al atoms and $^{15}NH_3$ gave a sextet of doublets of poorly resolved doublets of doublets. The latter features could be simulated by using the parameters $a_{15}(1) = 37$ MHz and $a_{\mathrm{H}}(1) = 27$ MHz with a line width of 8 MHz.



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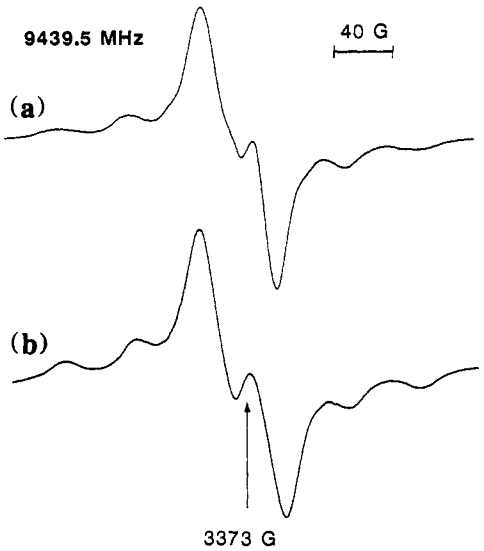
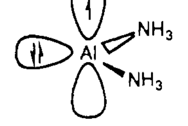


Figure 4. (a) The central feature (D) of the spectrum from Al and ND_3 in adamantane at 77 K that is assigned to $Al(NH_3)_2$ and (b) a simulation of the central feature by using the parameters given in the text for $Al(NH_3)_2$ superimposed on a broad feature with $a_{\mathrm{Al}} = 20$ MHz and $g = 1.9999$.

Dividing the observed Al hfi for species B by $A = 3911$ MHz gives $\rho_{3s} = 0.24$ and the H hfi by $A = 1400$ MHz[18] gives $\rho_{1s} = 0.16$ for a total unpaired s spin population of 0.40. Most of the remaining unpaired spin is probably located in an Al 3p orbital but could not be estimated because of the isotropic nature of the spectrum.

Spectrum C: The most intense features in the overall spectrum were the central features, C, which are not shown in Figure 1 because they were off scale at the receiver gain needed to give reasonably intense spectra of A, B, and D. A representative spectrum of C is shown in Figure 4, for reaction of Al with ND_3. The spectrum from Al and NH_3 was similar but not as well resolved. There were clearly six lines in the spectrum and their shape suggested a highly anisotropic Al hfi from a species with one Al nucleus. These six parallel features were readily measured to give $a_{\parallel}(\mathrm{Al}) = 131.5$ MHz and $g_{\parallel} = 1.999$. The overall shape of the spectrum was very similar to the spectra given by $Al(CO)_2$[13] and $Al[C_2H_4]_2$[7] and the carrier was probably $Al(NH_3)_2$. Spectral simulation (Figure 4b) suggested $a_{\perp}$ is ca. 20 MHz which means that $A_{\mathrm{iso}} = 57.2$ MHz and $A_{\mathrm{dip}} = 30.5$ MHz. The unpaired spin populations are therefore $\rho_{3s} = 0.01$ and $\rho_{3p} = 0.37$. Bonding in this species probably involves donation of the lone-pair electrons from the NH_3 ligands into sp^2-hybridized orbitals on the metal center with two electrons in the remaining hybridized orbital and the odd electron in the p_z orbital as shown in structure **4**.



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Codeposition of Al atoms with neat NH_3 gave an olive-green deposit that gave only the EPR spectrum that has been assigned to $Al(NH_3)_2$. This may be because the seven-electron species $Al(NH_3)_2$ is thermodynamically more stable than the eleven-electron species $Al(NH_3)_4$. The insertion product $HAlNH_2$ was also not detected in this system perhaps because of the influence of the NH_3 concentration on its formation.

Spectrum D: Spectrum B was perturbed by a second spectrum that could best be analyzed as a sextet of doublets and is labeled in Figure 1 as spectrum D. The doublet components of D are most

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Table I. EPR Parameters of the Products from Reaction of Al Atoms with NH_3 in Adamantane at 77 K[a]

species	$a_{\parallel}$ (Al)	$a_{\perp}$ (Al)	a_H	a_N	$g_{\parallel}$	$g_{\perp}$
$Al(NH_3)_4$ (**A**)	786.3	786.3		23.0	1.9997	1.9997
$HAlNH_2$ (**B**)	922.5	922.5	228.7 27[b]	27	2.0003	2.0003
$Al(NH_3)_2$ (C)	131.5	ca. 20			1.9990	1.9990
HAlOH (D)	911.3	911.3	286.4		1.9998	1.9998

[a] Hyperfine interactions in MHz. [b] Hfi of one of the amino hydrogens.

readily seen overlapping the $M_1 = \pm^3/_2$ lines of **B**. An exact solution of the Breit–Rabi equation for D gave $a_{Al} = 911.3 \pm 1.06$ MHz, $a_H = 286.4 \pm 3.7$ MHz, and $g = 1.9998 \pm 0.0004$. These parameters are close enough to those of HAlOH ($\langle a_{Al} \rangle = 921$ MHz, $a_H = 282$ MHz, and $\langle g \rangle = 2.0007$) that we can assign spectrum D to this species. Knight and co-workers[25] have suggested that HAlOH has a charge distribution and electronic structure that can be described as AlH^+OH^- with 90% of the unpaired electron on the AlH^+ fragment. HAlOH must be formed by reaction of Al atoms with adventitious H_2O.[8,25]

Further evidence for the identity of D was obtained from the reaction of ground-state Al atoms with D_2O in adamantane at 77 K which resulted in the formation of DAlOD with the parameters $a_{Al} = 907.8 \pm 0.78$ MHz, $a_D(1) = 44.8 \pm 2.3$ MHz, and $g = 1.9990 \pm 0.0004$.

Annealing Experiments: $Al(NH_3)_2$, $HAlNH_2$, and $Al(NH_3)_4$ in adamantane disappeared rapidly when samples were warmed above 150 K, but we were not able to determine the relative stabilities from these experiments because the spectrum of $Al(NH_3)_2$ was much more intense than those of $HAlNH_2$ and $Al(NH_3)_4$. A narrow line ($\Delta H_{pp} = 13.5$ G) centered at $g = 1.9998$ was the only signal that remained above this temperature. This line was much broader than the single line ($\Delta H_{pp} = 1.6$ G) that was obtained when samples of Al and ND_3 in adamantane were warmed above 150 K. These line widths are consistent with a trapped electron interacting with ammonia although the g factor seems low.[16]

Conclusions. Reaction of ground-state Al atoms with NH_3 in adamantane at 77 K gives at least three transient mononuclear Al(0) paramagnetic products, $Al(NH_3)_4$, $HAlNH_2$, and $Al(NH_3)_2$. These are probably the initial products in the production of amide and hydrogen from Al atoms and NH_3.

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Registry No. A, 137696-26-5; B, 81719-10-0; C, 137696-27-6; D, 73113-59-4; Al, 7429-90-5; NH_3, 7664-41-7.

Application and Evaluation of ab Initio Chemical Shift Calculations for Boranes and Carboranes. How Reliable Are "Accurate" Experimental Structures?[†]

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Abstract: The ^{11}B chemical shifts of the boranes B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12}, the borane anions $B_2H_7^-$, $B_3H_8^-$, $B_4H_9^-$, and the carboranes 1,3-$C_2B_2H_4$, 1,5-$C_2B_3H_5$, 1-CB_5H_7, 1,6-$C_2B_4H_6$, 1,2-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, 1,2-$C_2B_3H_7$, 2-CB_5H_9, 2,3-$C_2B_4H_8$, 2,3,4-$C_3B_3H_7$, and 2,3,4,5-$C_4B_2H_6$ have been calculated using the IGLO (individual gauge for localized orbitals) method. Three sets of ab initio geometries have been employed, 3-21G, 6-31G*, and MP2/6-31G*. For the geometries optimized ab initio at a correlated level (MP2/6-31G*), the agreement with the experimental values is excellent in the case of the binary boron hydrides (standard deviation 1.4 ppm) and acceptable in the case of the carboranes (standard deviation 3.3 ppm). The IGLO chemical shifts, calculated using the experimental geometries recommended in Beaudet's recent compilation, gave significantly poorer results than the MP2/6-31G* geometries. For B_8H_{12}, an alternative assignment of the observed boron resonances is supported by the IGLO calculations. The effect of counterions on geometry and chemical shifts of $B_3H_8^-$ is shown to be very small. No relationship between ^{11}B chemical shifts and calculated atomic charges is apparent.

Introduction

The structures of polyhedral boranes challenged the chemists for many years, until the Lipscomb group solved the essential nature of these species.[1] In his recent critical review, "The Molecular Structures of Boranes and Carboranes",[2] R. A. Beaudet summarized the best currently available structural data for these compounds, based on X-ray structure analysis, gas-phase electron diffraction, and microwave spectroscopy. He presented recommended sets of cartesian coordinates for 31 molecules, including the principal boranes and carboranes, and pointed out that accurate structural data are essential for a refined knowledge of the bonding in electron-deficient molecules. I. and M. Hargittai also recently emphasized "The Importance of Small Structural Differences",[3] and included quantum chemical calculations as an additional source of structural information. Indeed, ab initio molecular orbital theory has become increasingly successful in predicting molecular structures and establishing their accuracy.[4,5] E.g., we have been using IGLO (individual gauge for localized orbitals)[6]

[†] A preliminary version of part of this work was included in a volume (cf. ref 10) dedicated to Prof. W. N. Lipscomb on the occasion of his 70th birthday; we also dedicate this paper to the pioneer in the structural elucidation of boron compounds.

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