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 $M_I = \pm^3/_2$ 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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chemical shift calculations to distinguish among structural alternatives for numerous carbocations.[7] Since the computed ^{13}C chemical shifts often are very sensitive to small geometric changes, the combined ab initio/IGLO/NMR method affords a valuable tool for structural investigations.

We have reported similar applications to boron compounds in preliminary communications. A C_1 form of B_5H_{11} was favored over the C_s geometry.[8] The deficiencies of the electron diffraction structure of B_6H_{12} were shown on the basis of the IGLO calculations.[9] We now examine a wider scope of polyhedral boron compounds[10] in order to test and to demonstrate the reliability of this approach.

As NMR spectroscopy is particularly useful in boron chemistry, much δ ^{11}B NMR data are available.[11] Theoretical calculations of boron chemical shifts have been reported, both at semiempirical[12] and at SCF levels.[13] The evaluation of the paramagnetic contributions usually is the critical problem. Recently, several ab initio methods for the calculation of NMR shifts have been developed[14] which are based on the coupled Hartree–Fock (CHF) theory. We have now applied the IGLO method to assess the quality of four different sets of borane and carborane geometries (experimental and ab initio at various theoretical levels). In the present systematic study we will show that ab initio calculated molecular structures are at least as accurate as those derived by experimental techniques.

Methods, Basis Sets and Geometries

The chemical shifts were calculated using the IGLO method.[6] Huzinaga[15] basis sets, recommended by the Bochum group,[6b] were employed which were contracted as follows:

Basis DZ	C,B	7s3p	contracted to [4111,21]
	H	3s	contracted to [21]
Basis II′	C	9s5p1d	contracted to [51111,2111,1] p-coefficient 1.0
	B	9s5p1d	contracted to [51111,2111,1] p-coefficient 0.5
	H		same as DZ

B_2H_6 was used as the primary reference, and the δ values were converted to the $BF_3{\cdot}OEt_2$ scale using the experimental value of $\delta(B_2H_6) = 16.6$ ppm.[16]

The geometries were optimized ab initio at the restricted Hartree–Fock (RHF) level using the GAUSSIAN 82,[17] GAUSSIAN 86,[18] and CADPAC[19] programs with standard basis sets[4,20] 3-21G, 6-31G*, and in one case 6-31G**. Electron correlation was included in terms of Møller–Plesset second-order perturbation theory.[21] CADPAC was employed for most of the MP2/6-31G* optimizations using analytical gradients.

The most of the experimental geometries that were employed for IGLO calculations were taken from the compilation by Beaudet.[2] These are a composite of the "best available structural data" and were provided conveniently in cartesian coordinate format. Beaudet also presented a comprehensive and critical evaluation of the experimental geometries. One should bear in mind that the different techniques (electron/X-ray diffraction, microwave spectroscopy, theoretical calculations) yield different structural parameters (r_g, r_s, r_e values, respectively). Hence, direct comparisons should always be made with caution.[22] The differences between these parameters, estimated by Beaudet to be less than ca. ±0.01 Å,[2] are often smaller than the discrepancies reported here. One referee has suggested that we take experimental errors into consideration and provide "a detailed examination of the experimental information". This has already been undertaken by Beaudet, and we refer readers to his review.[2]

Results

General Performance of IGLO Calculations. The structural parameters for **1**–**21** are summarized in Table I (for numbering see Figures 1 and 2) and are compared with the experimental geometries, if available. The IGLO calculated ^{11}B chemical shifts are presented in Table II together with the experimental NMR data. Figures 3a–f shows plots of the calculated vs the experimental ^{11}B chemical shifts; the results of statistical analysis are presented in Table III.

In Figure 3a, the IGLO values are calculated employing the experimental geometries. The agreement between calculated and experimental ^{11}B chemical shifts is only modest. For some compounds (B_6H_{12}, 1,2-$C_2B_3H_7$, 1-CB_5H_9), exceptionally large deviations of ca. 15–19 ppm are noted.

The computed energy of a structure might be an additional criterion for its accuracy. In Table IV, single point calculations at the MP2(full)/6-31G* level for the experimental geometries are compared to the ab initio optimized energies at the same level. While most of the gas-phase determined structures are only a few kcal/mol higher in energy as compared to the ab initio geometries, the X-ray derived geometries of B_6H_{10} and B_8H_{12} perform somewhat more poorly (ca. 28 kcal/mol less stable than the optimized structures). Exceptionally high relative energies (30–60 kcal/mol) are computed for the experimental structures of B_6H_{12}, $C_2B_3H_7$, and CB_5H_9. As pointed out above, these also show the largest deviations of IGLO vs experimental chemical shifts. The apparent imperfections of these geometries will be discussed later.

In Figure 3b,c, the geometries employed in the IGLO calculations were optimized ab initio at Hartree–Fock levels, using 3-21G and 6-31G* basis sets, respectively. The overall performance is comparable to that of the experimental geometries in Figure 3a. Many of the computed δ values are shifted more or less pronounced to higher field. Relatively large deviations are found for 1,5-$C_2B_3H_5$ and 1-CB_5H_7 (see below).

Figure 3d,e shows the same plots for MP2/6-31G* optimized geometries, using DZ and II′ basis sets, respectively, in the IGLO calculations. Here, the agreement is quite good (standard deviation for all points ca. 3 ppm, correlation coefficient over 0.99). At the highest theoretic level employed, II′//MP2/6-31G*, only the

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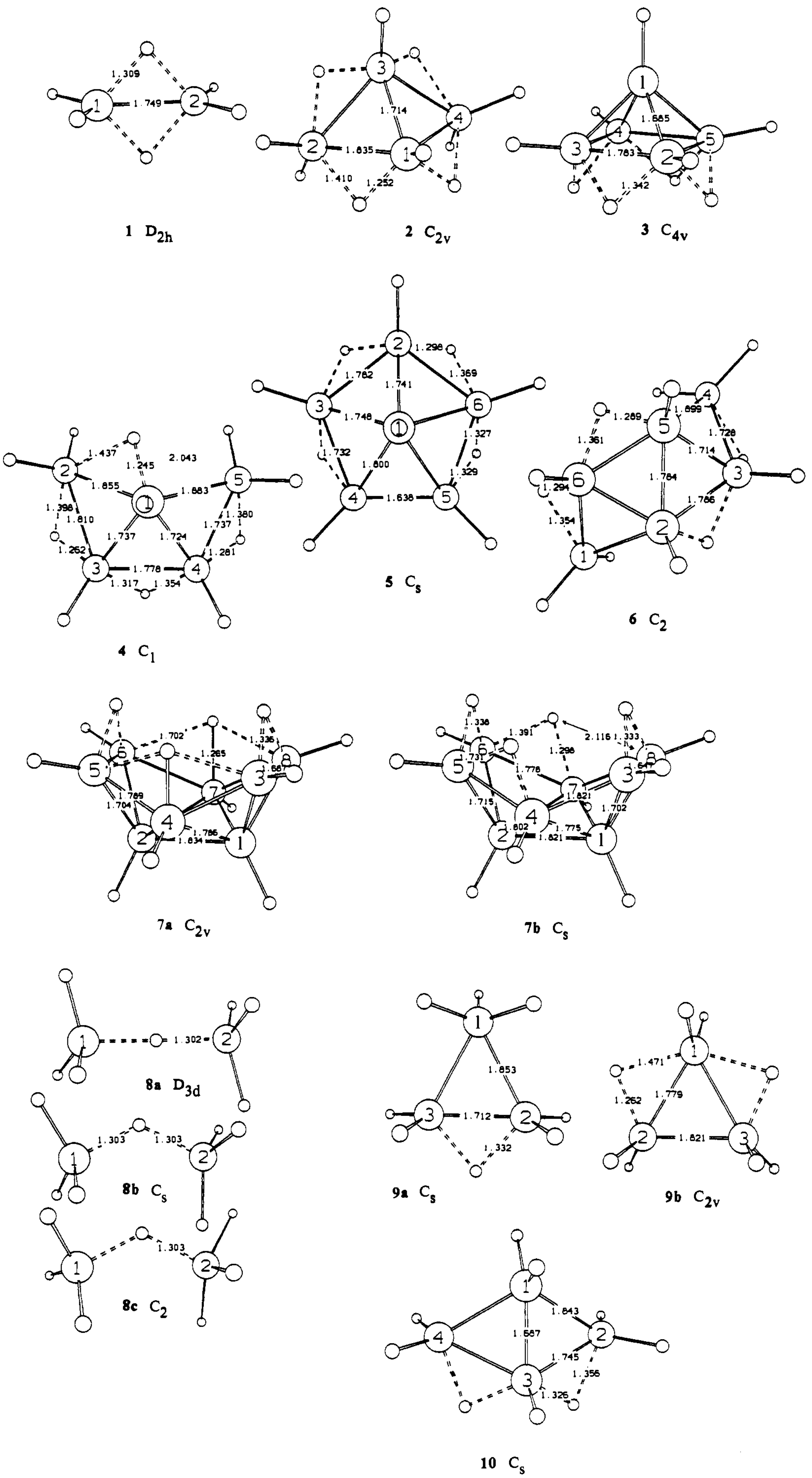

1 D_{2h} **2** C_{2v} **3** C_{4v}

4 C_1 **5** C_s **6** C_2

7a C_{2v} **7b** C_s

8a D_{3d}

8b C_s

8c C_2

9a C_s **9b** C_{2v}

10 C_s

Figure 1. Structures of the binary boranes (**1–10**). The bond distances refer to the MP2/6-31G* optimized structures.

Table I. Geometric Parameters for **1–21** (Bond Distances in Å)[ee]

B_2H_6 (**1**)

	B1B2	B1Hb		B1B2	B1Hb
3-21G	1.785	1.315	*exptl (IR)*[a]	*1.743*	*1.314*
6-31G*	1.779	1.316	*exptl (GED)*[b]	*1.775*	*1.339*
MP2/6-31G*	1.749	1.309			

B_4H_{10} (**2**)

	B1B2	B1B3	B1H13	B2H13		B1B2	B1B3	B1H13	B2H13
3-21G	1.902	1.733	1.248	1.430	MP2/6-31G**	1.838	1.715	1.245	1.405
6-31G*	1.893	1.741	1.247	1.423	*exptl (MW)*[c]	*1.854*	*1.718*	*1.428*	*1.425*
MP2/6-31G*	1.835	1.714	1.252	1.410	*exptl (GED)*[d]	*1.856*	*1.704*	*1.315*	*1.484*

B_5H_9 (**3**)

	B1B2	B2B3	B2H23		B1B2	B2B3	B2H23
3-21G	1.709	1.827	1.349	MP2/6-31G*	1.685	1.783	1.342
6-31G*	1.702	1.811	1.345	*exptl (MW)*[e]	*1.690*	*1.803*	*1.352*

B_5H_{11}[f] (**4**)

	B1B2	B1B3	B1B4	B1B5	B2B3	B3B4	B4B5
3-21G	1.893	1.795	1.772	1.952	1.835	1.852	1.762
6-31G*	1.896	1.761	1.758	1.939	1.856	1.830	1.750
MP2/6-31G*	1.855	1.737	1.724	1.883	1.810	1.778	1.737
exptl (X-ray)[g]	*1.870*	*1.720*	*1.720*	*1.870*	*1.760*	*1.770*	*1.760*
exptl (GED)[h]	*1.891*	*1.741*	*1.741*	*1.891*	*1.812*	*1.760*	*1.812*

B_5H_{11} (**4**)

	B1Hb	B2Hb	B5Hb	B2H23	B5H45	B3H23	B4H45	B3H34	B4H34
3-21G	1.229	1.549	1.993	1.477	1.472	1.236	1.254	1.323	1.336
6-31G*	1.235	1.459	2.134	1.443	1.410	1.243	1.266	1.318	1.351
MP2/6-31G*	1.245	1.437	2.043	1.398	1.380	1.262	1.281	1.317	1.345
exptl (X-ray)[g]	*1.090*	*1.670*	*1.670*	*1.300*	*1.300*	*1.220*	*1.220*	*1.180*	*1.180*
exptl (GED)[h]	*1.327*[i]	*1.594*	*1.898*	*1.394*	*1.394*	*1.274*	*1.274*	*1.335*	*1.335*

B_6H_{10} (**5**)

	B1B2	B1B3	B1B4	B2B3	B3B4	B4B5	B2H23	B3H23	B3H34	B4H34
3-21G	1.756	1.773	1.863	1.819	1.773	1.629	1.291	1.377	1.312	1.375
6-31G*	1.761	1.765	1.844	1.824	1.760	1.637	1.292	1.376	1.314	1.345
MP2/6-31G*	1.741	1.748	1.800	1.782	1.732	1.638	1.298	1.369	1.327	1.329
exptl (X-ray)[j]	*1.736*	*1.753*	*1.795*	*1.794*	*1.737*	*1.596*	*1.32*	*1.48*	*1.31*	*1.35*
exptl (MW)[k]	*1.774*	*1.762*	*1.783*	*1.818*	*1.710*	*1.654*				

B_6H_{12}[l] (**6**)

	B1B2	B1B6	B2B3	B2B5	B2B6	B1H16	B6H16	B2H23	B3H23
3-21G	1.939	1.761	1.829	1.792	1.741	1.388	1.273	1.291	1.357
6-31G*	1.941	1.747	1.825	1.798	1.738	1.376	1.283	1.291	1.357
MP2/6-31G*	1.899	1.728	1.786	1.784	1.714	1.354	1.294	1.289	1.361
exptl (GED)[m]	*1.778*	*1.913*	*1.699*	*1.821*	*1.777*	*1.416*	*1.200*	*1.308*	*1.308*

B_8H_{12} (**7a**)

	B1B2	B1B4	B2B4	B1B3	B2B5	B3B4	B6B7	B3B8	B5B6
3-21G	1.877	1.828	1.828	1.719	1.719	1.823	1.823	1.709	1.709
6-31G*	1.884	1.817	1.817	1.706	1.706	1.819	1.819	1.699	1.699
MP2/6-31G*	1.834	1.786	1.786	1.704	1.704	1.789	1.789	1.687	1.687
B_8H_{12} (**7b**)									
3-21G	1.835	1.812	1.847	1.732	1.747	1.835	1.818	1.662	1.764
6-31G*	1.837	1.799	1.885	1.714	1.738	1.850	1.811	1.649	1.757
MP2/6-31G*	1.821	1.775	1.802	1.702	1.715	1.821	1.778	1.647	1.731
exptl (X-ray)[n]	*1.830*	*1.792*	*1.808*	*1.710*	*1.720*	*1.822*	*1.806*	*1.684*	*1.705*

B_8H_{12} (**7a**)

	B4H45	B5H45	B3H45	B3H38	B5H56
3-21G	1.258	1.763	1.763	1.343	1.343
6-31G*	1.252	1.748	1.748	1.340	1.340
MP2/6-31G*	1.265	1.702	1.702	1.336	1.336
B_8H_{12} (**7b**)					
3-21G	1.313	1.347	2.238	1.345	1.336
6-31G*	1.310	1.350	2.256	1.341	1.338
MP2/6-31G*	1.298	1.391	2.116	1.333	1.338
exptl (X-ray)[n]	*1.287*	*1.496*	*2.021*	*1.322*	*1.300*

Table I (Continued)

$B_2H_7^-$

	8a	**8b**			**8c**	
	B1Hb	B1Hb	B2Hb	B–H–B	B1–Hb	B–H–B
6-31G*[o]	1.329	1.329	1.329	141.2°	1.328	140.8°
MP2/6-31G*[o]	1.303	1.303	1.303	127.0°	1.302	126.7°
MP2/6-31G**		1.297	1.297	127.3°	1.298	126.4°
exptl (X-ray)[p]		*1.00*	*1.27*	*136.4°*		
exptl (neutron-diff)[q]		*1.21*	*1.32*	*127.2°*		

$B_3H_8^-$

	9a			**9b**			
	B1B2	B2B3	B2H23	B1B2	B2B3	B1H12	B2H23
3-21G	1.962	1.728	1.338	1.810	1.923	1.576	1.255
6-31G*	1.940	1.718	1.337	1.798	1.907	1.543	1.254
MP2/6-31G*	1.853	1.712	1.332	1.779	1.821	1.471	1.262
exptl (X-ray)[r]				*1.77*	*1.80*	*1.50*	*1.20*
exptl (X-ray)[s]				*1.784*	*1.832*		

$B_4H_9^-$ (**10**)

	B1B2	B2B3	B1B3	B2H23	B3H23
3-21G	1.863	1.790	1.732	1.393	1.309
6-31G*	1.884	1.765	1.713	1.366	1.333
MP2/6-31G*	1.843	1.745	1.687	1.356	1.326

	1,3-$C_2B_2H_4$ (**11**)			1,5-$C_2B_3H_5$ (**12**)	
	BC	CC	α^t	BC	BB
3-21G	1.521	1.883	47.6°	1.583	1.945
6-31G*	1.500	1.787	50.8	1.555	1.886
MP2/6-31G*	1.501	1.787	53.1°	1.550	1.838
exptl[u]	*1.504*	*1.814*	*52°*	*1.556*	*1.853*

1,2-$C_2B_3H_7$ (**13**)

	C1C2	B1B3	C1B4	C2B3	B3B4
3-21G	1.701	1.647	1.595	1.535	1.918
6-31G*	1.620	1.614	1.572	1.525	1.871
MP2/6-31G*	1.604	1.608	1.562	1.535	1.836
exptl[v]	*1.453*	*1.612*	*1.734*	*1.680*	*1.707*

1-CB_5H_7 (**14**)

	C1B2	C1B4	B2B3	B2B5	B2B6	B4B5	B4B6	B2Hb	B6Hb
3-21G	1.629	1.646	1.857	1.749	2.026	1.780	1.692	1.353	1.857
6-31G	1.600	1.626	1.857	1.712	1.920	1.728	1.693	1.367	1.591
MP2/6-31G*	1.596	1.626	1.858	1.696	1.871	1.717	1.696	1.389	1.475
exptl (MW)[w]	*1.600*	*1.632*	*1.872*	*1.704*	*1.888*	*1.716*	*1.697*		
exptl (GED)[x]	*1.602*	*1.659*	*1.921*	*1.685*	*1.909*	*1.756*	*1.689*	*1.329*	*1.397*

	1,6-$C_2B_4H_6$ (**15**)		1,2-$C_2B_4H_6$ (**16**)				
	C1B2	B2B3	C2C3	B1C2	B5C2	B1B5	B4B5
3-21G	1.648	1.741	1.587	1.635	1.661	1.773	1.708
6-31G*	1.619	1.709	1.537	1.609	1.627	1.738	1.703
MP2/6-31G*	1.619	1.705	1.533	1.615	1.623	1.724	1.707
exptl (GED)[y]	*1.634*	*1.724*	*1.535*	*1.621*	*1.618*	*1.723*	*1.745*

2-CB_5H_9 (**17**)

	B1C2	B1B3	B1B4	C2B3	B3B4	B4B5	B3H34	B4H34	B4H45
3-21G	1.802	1.857	1.759	1.507	1.804	1.845	1.378	1.287	1.326
6-31G*	1.755	1.823	1.760	1.502	1.787	1.838	1.370	1.292	1.326
MP2/6-31G*	1.731	1.791	1.738	1.511	1.757	1.797	1.352	1.303	1.327
exptl (partial MW)[z]		*1.782*	*1.781*		*1.759*	*1.830*			

2,3-$C_2B_4H_8$ (**18**)

	B1C2	B1B4	B1B5	C2C3	C2B6	B5B6	B5H56	B6H56
3-21G	1.848	1.819	1.731	1.417	1.521	1.820	1.325	1.323
6-31G*	1.770	1.801	1.735	1.411	1.515	1.805	1.330	1.317
MP2/6-31G*	1.737	1.773	1.722	1.426	1.520	1.773	1.334	1.312
exptl[aa]	*1.750*	*1.772*	*1.715*	*1.418*	*1.499*	*1.790*	*1.308*	*1.280*

2,3,4-$C_3B_3H_7$ (**19**)

	B1C3	B1C2	B1B6	C2C3	C2B6	B5B6	B5H56
3-21G	1.854	1.799	1.786	1.421	1.537	1.818	1.323
6-31G*	1.755	1.737	1.775	1.413	1.531	1.789	1.320
MP2/6-31G*	1.729	1.718	1.754	1.426	1.532	1.760	1.319

Table I (Continued)

2,3,4,5-$C_4B_2H_6$ (**20**)

	B1C3	B1C2	B1B6	C3C4	C2C3	C2B6
3-21G	1.783	1.753	1.921	1.410	1.449	1.541
6-31G*	1.716	1.713	1.856	1.405	1.433	1.528
MP2/6-31G*	1.701	1.701	1.821	1.424	1.439	1.528
exptl (MW)[bb]	*1.697*	*1.709*	*1.886*	*1.424*	*1.436*	*1.541*

2,4-$C_2B_5H_7$ (**21**)

	B1B3	B1C2	B1B5	B3C2	C2B6	B5B6
3-21G	1.907	1.757	1.818	1.555	1.590	1.669
6-31G*	1.850	1.718	1.799	1.536	1.565	1.652
MP2/6-31G*	1.824	1.704	1.793	1.541	1.559	1.645
exptl (MW)[cc]	*1.818*	*1.708*	*1.816*	*1.546*	*1.565*	*1.651*
exptl (GED)[dd]	*1.852*	*1.717*	*1.772*	*1.524*	*1.556*	*1.659*

[a] High-resolution IR spectroscopy, r_e values, ref 23. [b] Bartell, L. S., Carrol, B. L. *J. Chem. Phys.* **1965**, *42*, 1135. [c] Reference 25a. [d] Reference 25b. [e] Reference 27. [f] Reference 8. [g] Levine, R. L.; Lipscomb, W. N. *J. Chem. Phys.* **1953**, *21*, 2087. [h] Reference 28. [i] Fixed. [j] Reference 31. [k] Reference 32. [l] Reference 11. [m] Reference 34. [n] Reference 36. [o] Reference 39. [p] Reference 40. [q] Reference 41. [r] Reference 43a. [s] Cs salt, the positions of the hydrogens have not been refined, ref 43b. [t] Puckering angle C1–B2–B4–C3. [u] **11**, ref 53; **12**, ref 55. [v] "Preliminary", ref 2. [w] Reference 59b. [x] Reference 59a. [y] **15**: Mastryukov, V. S.; Dorofeeva, O. V.; Vilkov, L. V.; Golubinski, A. V.; Zhigach, A. F.; Laptev, V. T.; Petrunin, A. B. *Russ. J. Struct. Chem.* (*Engl. Transl.*) **1975**, *16*, 159. **16**: Beaudet, R. A.; Poyntner, R. L. *J. Chem. Phys.* **1970**, *53*, 1899. [z] No carbon positions were refined, ref 63. [aa] Boer, P. F.; Streib, W. E.; Lipscomb, W. N. *Inorg. Chem.* **1964**, *3*, 1666. [bb] Pasinski, B. P.; Beaudet, R. A. *J. Chem. Phys.* **1974**, *61*, 683. [cc] Reference 66. [dd] Reference 67. [ee] The experimental values refer to the r_g (X-ray, GED) and r_s (MW) values, cf. ref 2.

values computed for the two carboranes 1,5-$C_2B_3H_5$ and 1,2-$C_2B_3H_7$ show large deviations from experiment (ca. 10 ppm, see below). If these compounds are excluded from the least-squares fit, the correlation is excellent: the slope is with 1.02 close to the ideal value, the correlation coefficient is 0.999, and the maximum and standard deviations are only 3.1 and 1.3 ppm, respectively.

As can be seen from the data in Table III, the performance of binary boron hydrides and carboranes is different: For the former, even geometries optimized at HF level give acceptable IGLO results, and the chemical shifts computed at the DZ//MP2/6-31* level without exception are in excellent accord with the experimental data (e.g., largest deviation 1.2 ppm).[10] For the carboranes, the degree of agreement is less convincing. It appears that—in order to obtain results comparable in quality to the boron hydrides—a somewhat higher level of theory is required. E.g., the performance of the 3-21G geometries is relatively poor (Figure 3b) with many of the chemical shifts being calculated at a field far too low. Also, the effect of employing a larger basis set in the IGLO calculations, which is less pronounced for the boron hydrides, seems more important in the case of the carboranes (Figure 3e,f, Table II). However, at the highest level of theory employed, II′//MP2/6-31G*, the agreement of computed and measured ^{11}B chemical shifts is excellent for all compounds of this study except for the two carboranes 1,5-$C_2B_3H_5$ and 1,2-$C_2B_3H_7$.

In the following, the results for individual molecules are discussed in more detail.

Neutral Boranes 1–8

B_2H_6 (1). Diborane(6), certainly the most important of all boron hydrides, served as the primary reference in the IGLO chemical shift calculations: the experimental structure[23] was taken as the standard. The IGLO ^{11}B chemical shifts for the various theoretical structures are in close agreement with experiment.[24] No pronounced dependence on the optimization level (Table II) is apparent. Hence, diborane is well suited to be used as the "theoretical reference". The IGLO results for B_2H_6 have been analyzed more detailed in terms of localized orbital contributions.[6b]

B_4H_{10} (2). It is known from experiment[25] that B_4H_{10} adopts a "butterfly" structure with overall C_{2v} symmetry. The geometrical parameters of the boron framework calculated at the MP2 level are in close agreement to those obtained from microwave spectroscopy (MW)[25a] and gas-phase electron diffraction (GED).[25b] However, there is some disagreement concerning the positions of the bridging hydrogens. In the ab initio structures, the B–H–B bridges are rather unsymmetric with close contacts to B1 and B3 (closer than measured in the GED study). In the MW investigation, one bridge-H coordinate could not be obtained.[25a] A more asymmetric B–H–B bridge would also fit the data, but the theoretical values still do not fall within the reported experimental error (ca. 0.02 Å for B–Hb lengths). While the IGLO $\delta^{11}B$ values for all structures are in reasonable accord with experiment, the best fit is found for the structures optimized at MP2 level.

For this relatively small and symmetric molecule we probed the effect of employing a larger basis set in the optimization (6-31G** which includes polarization functions on hydrogen). The MP2/6-31G* and MP2/6-31G** optimizd geometrical parameters do not show significant differences. Consequently, the chemical shifts calculated for these geometries are nearly identical. In contrast to many carbocation structures,[7] no polarization functions on hydrogen need to be used in the optimizations of boron hydrides.[26]

B_5H_9 (3). The calculated geometrical parameters and the chemical shifts of B_5H_9 do not show a pronounced dependence on the optimization level. The experimental geometry recommended by Beaudet (MW)[27] as well as the best theoretical structure (MP2/6-31G*) perform nearly equally well: both are comparable in energy (Table IV) and have similar IGLO chemical shifts (Table II).

B_5H_{11} (4). It is known both from experimental[28] and theoretical[8,29] investigations, that the unique bridging hydrogen in B_5H_{11} prefers an unsymmetric location, resulting in overall C_1 symmetry. The best theoretical structure for **4**—optimized at the MP2/6-31G* level—shows the critical hydrogen H_b to be involved in a perfectly normal, unsymmetrical B–H–B bond. Hence, the "styx" formulation[1] of B_5H_{11} should be 4112 rather than 3203. The barrier for the tautomerization of this unique hydrogen, proceeding through a transition state of C_s symmetry, was calculated to very low (about 1 kcal/mol at MP4sdtq/6-31G*//6-31G* + ZPE). The IGLO values computed for this transition-state geometry, however, showed pronounced deviations from experiment (up to ca. 8 ppm at DZ//MP2/6-21G*).

The IGLO δ ^{11}B values calculated for the ab initio structures of **4** are very sensitive to the "quality" of the geometry. With increasing level of theory employed in the optimization, the

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(23) Duncan, J. L.; Harper, *Mol. Phys.* **1984**, *51*, 371.

(24) Onak, T. P.; Landesman, H. L.; Williams, R. E.; Shapiro, I. *J. Phys. Chem.* **1959**, *63*, 1533.

(25) (a) Simmons, N. P. C.; Burg, A. B.; Beaudet, R. A. *Inorg. Chem.* **1981**, *20*, 533. (b) Dain, C. J.; Downs, A. J.; Laurenson, G. S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1981**, 472.

(26) Not even energies are affected very much, see, e.g., a study of B_3H_9: Stanton, J. F.; Lipscomb, W. N.; Bartlett, R. J.; McKee, M. L. *Inorg. Chem.* **1989**, *28*, 109.

(27) Schowch, D.; Burg, A. B.; Beaudet, R. *Inorg. Chem.* **1977**, *16*, 3219.

(28) Greatrex, R.; Greenwood, N. N.; Rankin, D. W.; Robertson, H. E. *Polyhedron* **1987**, *6*, 1849.

(29) McKee, M. L. *J. Phys. Chem.* **1989**, *93*, 3426.

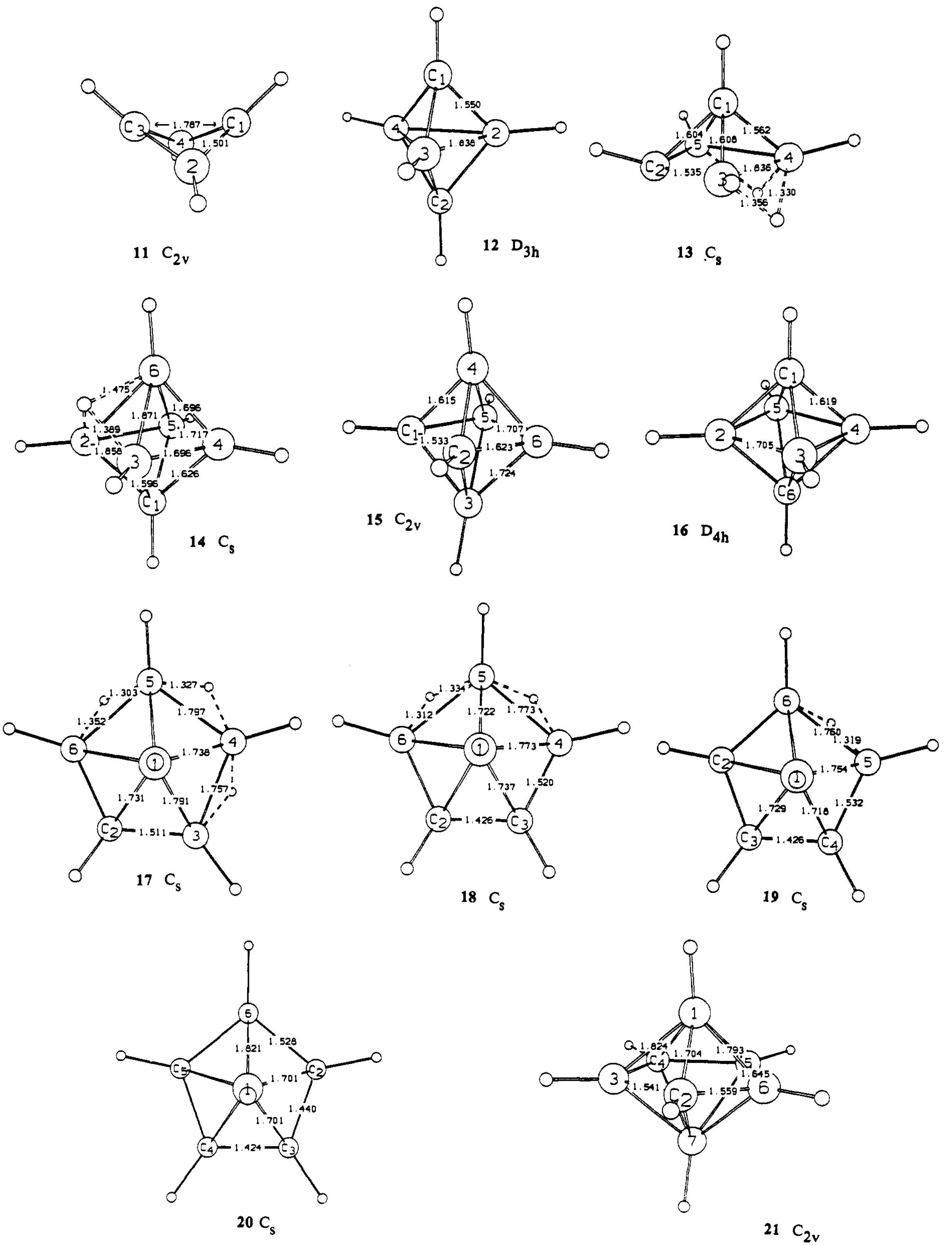

Figure 2. Structures of the carboranes **11**–**21**. The bond distances refer to the MP2/6-31G* optimized structures.

chemical shifts steadily approach the experimental values. Those for the MP2/6-31G* geometry are in excellent agreement with experiment.

The individual chemical shifts of B3 and B4 in **4** are calculated to be very different (−13.5 and +10.3 ppm), even though these atoms are not directly associated with the "critical" hydrogen (cf. B_8H_{12} below). This emphasizes the general importance of the exact positions of bridging hydrogens. The pronounced chemical shift difference between B3 and B4 to a large extent is due to the unsymmetric location of H_b: in the refinement of the experimental GED structure, the whole molecule with the exception of H_b was constrained to have C_s symmetry (cf. Table I). Despite a smaller "displacement" of H_b from the symmetric position (as compared to the theoretical structures), the calculated δ values of B3 and B4 also show a pronounced difference (−7.5 and +1.4 ppm).

B_6H_{10} (**5**). At room temperature, the molecule is fluxional due to a rapid tautomerization of the bridging hydrogens.[30] Thus,

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(30) Brice, V. T.; Johnson II, H. D.; Shore, S. G. *J. Chem. Soc., Chem. Commun.* **1972**, 1128. *J. Am. Chem. Soc.* **1973**, *95*, 6629.

Table II. IGLO $\delta^{11}B$ Chemical Shifts (in ppm rel $BF_3 \cdot OEt_2$)

	B_2H_6 (**1**)	B_4H_{10} (**2**)		B_5H_9 (**3**)	
		B1,3	B2,4	B1	B(2–5)
DZ//exptl[a]	16.6	−37.6	−3.9	−52.9	−9.0
DZ//3-21G	15.9	−41.6	−2.5	−55.0	−9.6
DZ//6-31G*	16.0	−41.7	−2.5	−55.9	−10.7
DZ//MP2/6-31G*	15.6	−42.4	−6.0	−55.2	−11.5
DZ//MP2/6-31G**		−42.7	−6.1		
II′//MP2/6-31G*	15.4	−40.0	−5.3	−55.1	−12.8
exptl[b]	*16.6*	*−41.8*	*−6.9*	*−53.1*	*−13.4*

B_5H_{11} (**4**)

	B1	B2	B5	ϕB2,5	B3	B4	ϕB3,4
DZ//exptl (X-ray)	−79.7			5.7			−5.0
DZ//exptl (GED)[c]	−58.1	6.5	15.8	11.1	−7.5	1.4	−3.1
DZ//3-21G	−51.6	14.5	23.3	18.8	−13.3	6.0	−3.7
DZ//6-31G*	−51.6	7.4	18.4	12.8	−15.5	8.8	−3.4
DZ//MP2/6-31G*	−55.8	1.4	12.8	7.1	−14.0	9.1	−2.6
II′//MP2/6-31G*	−53.9	2.2	13.7	8.0	−13.5	10.3	−1.6
exptl[d]	*−55.3*			*7.4*			*0.5*

B_6H_{10} (**5**)

	B1	B2	B3,6	B4,5
DZ//exptl	−45.3	−8.4	26.6	28.1
DZ//3-21G	−52.6	−7.6	18.0	22.8
DZ//6-31G*	−53.2	−7.4	18.5	21.5
DZ//MP2/6-31G*	−53.4	−7.2	18.0	19.5
II′//MP2/6-31G*	−51.5	−7.4	18.8	19.9
exptl[e]	*−51.8*	*−6.5*	*18.6*	*18.6*

B_6H_{12} (**6**)

	B1,4	B3,6	B2,5
DZ//exptl[f]	14.1	41.1	−13.3
DZ//3-21G	14.5	22.5	−22.1
DZ//6-31G*	12.9	21.6	−22.4
DZ//MP2/6-31G*	9.6	22.9	−23.0
II′//MP2/6-31G*	10.1	23.5	−22.8
exptl[b]	*7.9*	*22.6*	*−22.6*

B_8H_{12} (**4a**)

	B1	B2	ϕB1,2	B3,8	B5,6	ϕB3,5,6,8	B4,7
DZ//3-21G			−17.4			14.1	−39.3
DZ//6-31G*			−16.1			12.8	−39.5
DZ//MP2/6-31G*			−19.1			9.8	−39.5
B_8H_{12} (**4b**)							
DZ//exptl	1.1	−35.9	−17.4	18.1	11.1	14.6	−31.4
DZ//3-21G	17.2	−44.2	−13.5	13.2	8.0	10.6	−15.7
DZ//6-31G*	14.4	−45.9	−15.8	11.9	7.1	9.5	16.0
DZ//MP2/6-31G*	7.9	−44.3	−18.2	10.3	6.0	8.2	−22.4
II′//MP2/6-31G*	9.3	−42.9	−16.8	11.7	7.0	9.4	−22.3
exptl[g]			*−22.0*			*7.5*	*−19.4*

$B_2H_7^-$

	8a	**8b**	**8c**
DZ//exptl (X-ray)[h]		−38.7	
DZ//exptl (neutron-diff)[i]		−26.2	
DZ//6-31G*	−13.3	−17.3	−17.3
DZ//MP2/6-31G*	−14.7	−22.9	−23.1
DZ//MP2/6-31G**		−23.3	−23.2
II′//MP2/6-31G*		−24.5	−24.7
exptl[j]		*−24.6*	

$B_3H_8^-$

	9a			**9b**		
	B1	B2,3	ϕB	B1	B2,3	ϕB
DZ//3-21G	−41.5	−1.1	−14.6	1.4	−37.1	−24.3
DZ//6-31G*	−42.7	−1.5	−15.9	−2.0	−38.4	−26.2
DZ//MP2/6-31G*	−48.4	−7.4	−21.1	−10.0	−42.5	−31.6
II′//MP2/6-31G*	−50.6	−7.5	−21.9	−9.3	−43.5	−32.0
exptl[k]						*−29.8*

	$B_4H_9^-$ (**10**)			1,3-$C_2B_2H_4$ (**11**)	
	B1	B2,4	B3	C	B
DZ//3-21G	−54.7	−4.5	−1.8	122.5	36.6
DZ//6-31G*	−52.5	−8.4	2.9	97.9	36.1
DZ//MP2/6-31G*	−54.9	−9.9	0.9	95.7	34.2
II′//MP2/6-31G*	−55.9	−11.0	3.0	92.7	37.2
exptl[l]	*−54.5*	*−10.2*	*0.8*		

1,5-$C_2B_3H_5$ (**12**)

	C	B
DZ//exptl	96.9	13.5
DZ//3-21G	96.5	20.5
DZ//6-31G*	94.9	16.0
DZ//MP2/6-31G*	96.9	12.0
II′//MP2/6-31G*	97.5	11.4
GIAO/6-31G*//MP2/6-31G*	87.6	11.2
exptl[m]	*103.3*	*1.4*

1,2-$C_2B_3H_7$ (**13**)

	C1	C2	B3,5	B4
DZ//"prelim exptl"	0.6	54.0	−3.0	−17.8
DZ//3-21G	−25.6	60.3	−6.7	−19.2
DZ//6-31G*	−27.4	65.5	−10.2	−16.4
DZ//MP2/6-31G*	−24.3	64.2	−12.7	−14.6
II′//MP2/6-31G*	−34.8	48.6	−13.6	−15.7
exptl[n]			*−21.7*	*−23.7*

1-CB_5H_7 (**14**)

	C1	B2,3	B4,5	B6
DZ//exptl	45.1	−20.0	−5.5	12.2
DZ//3-21G	42.9	−17.7	0.8	24.6
DZ//6-31G*	45.5	−19.6	−6.9	12.0
DZ//MP2/6-31G*	49.9	−18.9	−7.9	5.2
II′//MP2/6-31G*	43.2	−20.6	−11.2	1.0
exptl[b]		*−19.0*	*−9.8*	*2.7*

	1,6-$C_2B_4H_6$ (**15**)		1,2-$C_2B_4H_6$ (**16**)		
	C1,6	B2,3,4,5	C1,2	B3,4	B5,6
DZ//exptl	78.8	−15.8	40.7	−13.4	9.8
DZ//3-21G	80.7	−15.5	46.1	−12.4	7.7
DZ//6-31G*	76.3	−17.0	42.6	−14.7	6.0
DZ//MP2/6-31G*	80.3	−18.1	44.5	−15.1	5.4
II′//MP2/6-31G*	71.7	−18.6	37.5	−15.3	1.4
exptl[p]	*78.5*	*−19.4*		*−16.3*	*1.6*

2-CB_5H_9 (**17**)

	C2	B1	B3,6	B4,5
DZ//exptl	119.5	−38.7	15.4	3.4
DZ//3-21G	103.2	−53.1	19.7	−5.8
DZ//6-31G*	98.9	−54.2	18.9	−4.3
DZ//MP2/6-31G*	105.3	−54.8	17.2	−3.7
II′//MP2/6-31G*	98.7	−52.6	17.5	−3.0
exptl[o]		*−51.9*	*16.6*	*−4.2*

2,3-$C_2B_4H_8$ (**18**)

	C2,3	B1	B4,6	B5
DZ//3-21G	128.6	−52.9	−1.4	−2.8
DZ//6-31G*	121.1	−56.1	0.0	−0.5
DZ//MP2/6-31G*	123.9	−56.3	−0.5	0.2
II′//MP2/6-31G*	119.5	−54.8	−1.6	0.4
exptl[q]	*122*	*−53.3*	*−2.0*	*0.1*

2,3,4-$C_3B_3H_7$ (**19**)

	C2,4	C3	B1	B5,6
DZ//3-21G	99.7	136.0	−53.9	−1.1
DZ//6-31G*	96.4	127.3	−57.6	−0.1
DZ//MP2/6-31G*	99.3	129.3	−57.9	−0.3
exptl (2,4-dimethyl-)[r]			*−51.6*	*−2.5*

Table II (Continued)

$2,3,4,5\text{-}C_4B_2H_6$ (**20**)

	C2,5	C3,4	B1	B6
DZ//3-21G	86.1	109.6	−60.3	15.5
DZ//6-31G*	86.2	104.2	−62.3	13.1
DZ//MP2/6-31G*	89.2	106.6	−62.3	11.7
II′//MP2/6-31G*	95.6	97.7	−62.1	10.9
exptl[s]			*−60.8*	*10.4*

$2,4\text{-}C_2B_5H_7$ (**21**)

	C2,4	B1,7	B3	B5,6
DZ//exptl	75.0	−19.1	6.2	4.6
DZ//3-21G	77.1	−15.9	12.8	4.0
DZ//6-31G*	73.9	−17.4	11.4	3.8
DZ//MP2/6-31G*	74.5	−17.9	10.7	3.4
II′//MP2/6-31G*	76.5	−21.7	8.1	3.3
exptl[t]	*80*	*−23.5*	*5.0*	*2.0*

[a] Unless otherwise noted, the experimental geometries employed in the IGLO calculations were taken from ref 2. [b] B_2H_6, ref 24. B_4H_{10}, B_6H_{12}: Jaworiwski, I. S.; Long, J. R.; Barton, L.; Shore, S. G. *Inorg. Chem.* **1979**, *18*, 56. B_5H_9: Tucker, P. M.; Onak, T.; Leach, J. B. *Inorg. Chem.* **1970**, *9*, 1430. [c] Reference 28. [d] Leach, J. B.; Onak, T.; Spielman, R.; Rietz, R. R.; Schaeffer, R.; Sneddon, G. L. *Inorg. Chem.* **1970**, *9*, 2170. [e] Reference 34. [f] Reference 34. [g] Reference 35, the assignment of the B1,2 and B4,7 resonances may be wrong, see text. [h] Reference 40. [i] Reference 41. [j] Reference 42. [k] Paine, R. T.; Fukushima, E.; Roeder, S. B. W. *Chem. Phys. Lett.* **1976**, *32*, 566. [l] Reference 50. [m] Grimes, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 1895. ^{13}C: ref 68. [n] Franz, D. A.; Grimes, R. N. *J. Am. Chem. Soc.* **1970**, *92*, 1438. [o] Groszek, E.; Leach, J. B.; Wong, G. T. F.; Ungermann, C.; Onak, T. *Inorg. Chem.* **1971**, *10*, 2770. [p] **15**: Onak, T.; Gerhardt, F. J.; Williams, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 5378. ^{13}C: ref 68. **16**: Onak, T.; Drake, R. P.; Dunks, G. B. *Inorg. Chem.* **1964**, *3*, 1686. [q] Akitt, J. W.; Savory, G. G. *J. Magn. Reson.* **1975**, *17*, 22. ^{13}C: ref 68. [r] Reference 64. [s] Onak, T. P.; Wong, G. T. F. *J. Am. Chem. Soc.* **1970**, *92*, 5226. [t] Warren, R.; Paquin, D.; Onak, T.; Dunks, G. B.; Spielman, J. R. *Inorg. Chem.* **1970**, *9*, 2285.

Table III. Statistical Analysis[a] of the Performance of IGLO Calculations (See Figure 3a–e)

IGLO basis//geometry	slope	correlation coefficient	deviation[b] largest	deviation[b] standard	plots figure
		Boron Hydrides			
DZ//exptl	1.08	0.984	18.5	5.3	3a
DZ//3-21G	1.02	0.990	10.4	5.5	3b
DZ//6-31G*	1.00	0.994	5.4	2.9	3c
DZ//MP2/6-31G*	1.01	0.999	3.1	1.2	3d
II′//MP2/6-31G*	1.01	0.999	2.2	1.4	3e
		Carboranes			
DZ//exptl	0.88	0.948	18.7	5.0	3a
DZ//3-21G	1.09	0.964	19.1	6.4	3b
DZ//6-31G*	1.08	0.984	14.6	4.2	3c
DZ//MP2/6-31G*	1.06	0.988	10.6	3.6	3d
II′//MP2/6-31G*	1.03	0.989	10.0	3.3	3e
		Boranes and Carboranes			
DZ//exptl	1.03	0.972	18.7	5.6	3a
DZ//3-21G	1.05	0.976	19.1	5.6	3b
DZ//6-31G*	1.03	0.985	14.6	4.2	3c
DZ//MP2/6-31G*	1.03	0.993	10.6	3.0	3d
II′//MP2/6-31G*	1.02	0.994	10.0	2.6	3e
without **12** and **13**:					
II′//MP2/6-31G*	1.02	0.999	3.1	1.3	

[a] Results of a least-squares analysis, IGLO vs experimental ^{11}B chemical shifts. [b] In ppm.

Table IV. Absolute (−au) and Relative Energies of ab Initio Optimized and of Experimental Geometries

compd		MP2/6-31G*// MP2/6-31G*[a]	MP2/6-31G*// Experiment[b]	E_{rel}[c]
1	B_2H_6	53.00228	53.00216	0.1
2	B_4H_{10}	104.86402	104.84957	9.1
3	B_5H_9	129.07812	129.07675	0.9
4	B_5H_{11}	130.21400	130.18441[d]	18.6
5	B_6H_{10}	154.43224	154.39079	26.0[g]
6	B_6H_{12}	155.57211	155.47810[e]	59.0
7b	B_8H_{12}	205.16537	205.12047	28.2[g]
8c	$B_2H_7^-$	53.60069	53.59294[f]	4.9
12	$C_2B_3H_5$	153.21102	153.21069	0.2
13	$C_2B_3H_7$	154.34820	154.29954	30.5[h]
14	CB_5H_7	165.92311	165.90969	8.4
15	$1,2\text{-}C_2B_4H_6$	178.58082	178.56873	7.6
16	$1,6\text{-}C_2B_4H_6$	178.59618	178.58873	4.7
17	CB_5H_9	167.09910	167.01751	51.2[i]
21	$C_2B_5H_7$	203.98407	203.98146	1.6

[a] MP2(full)/6-31G* optimized energies. [b] MP2(full)/6-31G* single point energies employing the experimental structures; unless otherwise noted, these were taken from ref 2. [c] Relative energy (kcal/mol) of the experimental geometries with respect to the ab initio structures. [d] Reference 27. [e] Reference 34. [f] Reference 41 (neutron-diffraction). [g] Experimental structure based on X-ray analysis. [h] "Preliminary" experimental structure from ref 2 (see text). [i] No carbon positions refined experimentally (see text).

the five basal boron atoms, B(2–6), are equivalent on the NMR time scale. At lower temperature, the single peak observed for B(2–6) is split into two resonances, which have been assigned to the static C_s structure **5** that is found in the solid state[31] and in the gas phase.[32] In this symmetry, three basal boron atoms are nonequivalent. Hence, two of these [(B3,6) and B(4,5)] must have nearly identical δ ^{11}B values. The IGLO chemical shifts for the ab initio geometries are in excellent accord with experiment, and B(3,6) and B(4,5) indeed have very similar δ ^{11}B values. In contrast to earlier predictions,[33] the substantial difference in the chemical shifts between these four borons and the other basal boron B2 is reproduced well by the IGLO calculations.

B_6H_{12} (**6**). A gas-phase electron diffraction (GED) study for this molecule has been reported recently which established the molecular C_2 symmetry.[34] However, on the basis of structural, energetic, and NMR criteria, the accuracy of the molecular dimensions derived by GED has been questioned.[9] As can be seen from the data in Table II, the IGLO δ ^{11}B values computed for the GED geometry do not agree at all with the experimental chemical shifts. The theoretical calculations are complicated somewhat by the existence of a high-lying "false" minimum at lower levels of theory.[9] However, the IGLO chemical shifts computed for the MP2/6-31G* geometry of **6**, the only minimum found at that level, are in excellent agreement with experiment. Hence, the geometric parameters calculated at the MP2/6-31G* level are probably more accurate than those derived by GED.

B_8H_{12} (**7**). On the NMR time scale, B_8H_{12} shows C_{2v} symmetry,[35] whereas this is reduced to C_s in the solid state (cf. **7b**).[36] Fluxional behavior in solution was considered involving two equivalent C_s structures. Beaudet suggested a gas-phase structure determination in order to confirm structural details of the "unaesthetic" C_s form.[2] Theoretical calculations by McKee reproduced the solid-state geometry quite well (3-21G basis set, see Table I) and predicted a very low barrier for the scrambling of the bridging hydrogens (C_{2v} transition state, cf. **7a**).[37] Our calculations, performed at a somewhat higher level of theory, reach the same conclusions: The MP2/6-31G* geometry of the C_s form **7b** is in good agreement with the X-ray structure. The

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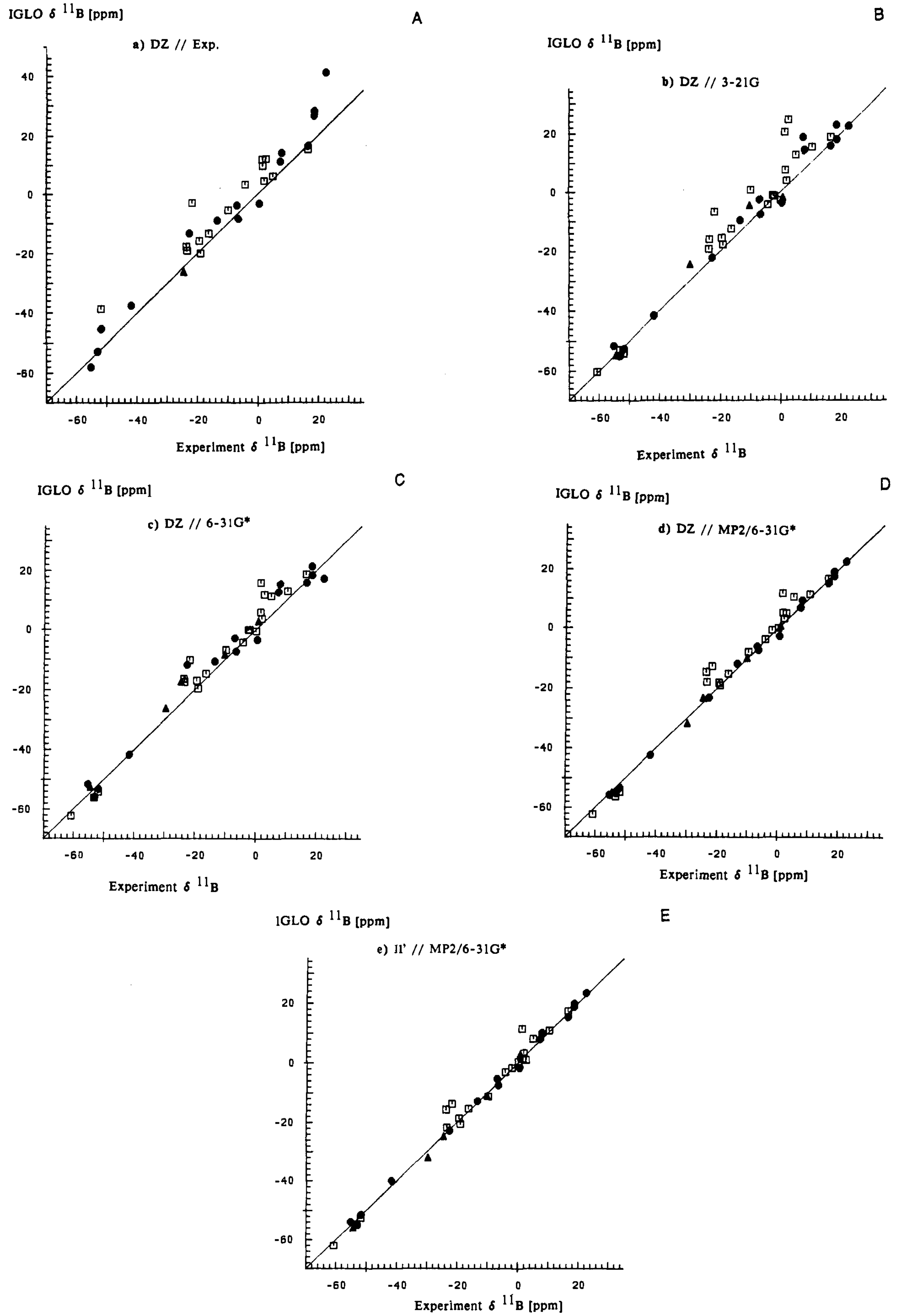

Figure 3. Comparison between IGLO calculated and experimental δ ^{11}B chemical shifts at various levels of theory, see text (circles, neutral boranes **1–6**; triangles, borane anions **8–10**; squares, carboranes **12–21**).

Table V: Mulliken (MPA) and Natural Population Analysis (NPA) Charges[a]

compd			MPA	NPA
1	B_2H_6		−0.014	−0.065
2	B_4H_{10}	$B_{1,3}$	−0.179	−0.341
		$B_{2,4}$	−0.096	−0.103
3	B_5H_9	B_1	0.038	0.092
		B_{2-5}	−0.157	−0.111
4	B_5H_{11}	B_1	−0.193	−0.406
		B_2	−0.092	−0.094
		B_5	−0.064	−0.053
		B_3	−0.141	−0.217
		B_4	−0.053	−0.135
5	B_6H_{10}	B_1	−0.013	−0.303
		B_2	−0.144	−0.187
		$B_{3,6}$	−0.129	−0.047
		$B_{4,5}$	−0.077	−0.151
6	B_6H_{12}	$B_{1,4}$	−0.078	−0.087
		$B_{2,5}$	−0.033	−0.092
		$B_{3,6}$	−0.146	−0.274
7b	B_8H_{12}	B1	0.089	−0.150
		B_2	−0.003	−0.262
		$B_{3,8}$	−0.096	−0.034
		$B_{4,7}$	−0.222	−0.261
		$B_{5,6}$	−0.115	−0.046
8c	$B_2H_7^-$		0.033	−0.199
9b	$B_3H_8^-$	B_1	0.050	−0.155
		$B_{2,3}$	−0.061	−0.446
10	$B_4H_9^-$	B_1	−0.080	−0.459
		$B_{2,4}$	−0.032	−0.179
		B_3	0.044	−0.192
11	$C_2B_2H_4$		0.202	0.497
12	$C_2B_3H_5$		0.115	0.435
13	$C_2B_3H_7$	B3,5	−0.043	0.158
		B4	−0.167	0.008
14	CB_5H_7	B2,3	−0.091	0.075
		B4,5	0.001	−0.009
		B6	−0.098	−0.015
15	1,2-$C_2B_4H_6$	B3,4	0.019	0.179
		B5,6	−0.002	0.055
16	1,6-$C_2B_4H_6$		0.016	0.179
17	CB_5H_9	B1	−0.004	−0.123
		B3,6	0.029	0.167
		B4,5	−0.160	−0.156
18	$C_2B_4H_8$	B1	0.009	0.016
		B4,6	0.010	0.043
		B5	−0.178	−0.121
19	$C_3B_3H_7$	B1	0.023	0.180
		B5,6	−0.004	0.039
20	$C_4B_2H_6$	B1	0.064	0.323
		B6	0.166	0.294
21	$C_2B_5H_7$	B1,7	0.011	0.231
		B3	0.126	0.334
		B5,6	0.085	0.041

[a] Calculated with 6-31G* basis set for MP2/6-31G* geometries.

"asymmetry" of the bridging hydrogens H45 and H67 with respect to the borons B3,5 and B6,8, respectively, is even larger in the MP2 geometry (1.391, 2.116 Å; X-ray: 1.469, 2.021 Å). Also, the H-bridged B3B8 bond (1.647 Å) is nearly as short as the unbridged B4B5 bond in B_6H_{10} (**5**, 1.638 Å, see Table I).

The C_{2v} form **7a** is only 3.0 kcal/mol higher in energy at MP2/6-31G*//MP2/6-31G*. This very low barrier is in accord with fluxionality on the NMR time scale.

The IGLO δ ^{11}B values for **7a** and **7b** in Table IV are most revealing: The chemical shifts computed employing the X-ray structure do not agree very well with experiment (ca. 10 ppm deviation). Also, the C_{2v} ab initio geometries do not perform satisfactory (20 ppm deviation at DZ//MP2/6-31G*).

The averaged IGLO values for the MP2/6-31G* geometry of **7b** give rise to the question whether the original assignment of the B(1,2) and B(4,7) resonances is correct. From the published data this assignment seems a little tentative. If the assignment for B(1,2) and B(4,7) is reversed, then the IGLO δ ^{11}B chemical shifts at the DZ//MP2/6-31G* level are in excellent agreement with the experimental values (in parentheses): −22.4 (−22.0), −18.2 (−19.4), and 8.2 (7.5) ppm. Since more experimental information appears to be needed in order to ascertain the assignments, the IGLO values for **7b** have not been included in the correlation of Figure 3 and Table III.

Interestingly, the computed individual chemical shifts for B1 and B2 in the static C_s form **7b** show large differences (7.9 and −44.3 ppm, DZ//MP2/6-31G* level). The same has been found for B3 and B4 in B_5H_{11} (see above). These theoretical values are in line with the observing, that a boron nucleus "opposite" to a B–H–B arrangement resonates at higher field than one "opposite" to unbridged B–B edge.[38] In the cases of B_5H_{11} and B_8H_{12}, however, the low scrambling barriers are likely to preclude the experimental confirmation of the predicted individual chemical shifts.

Borane Anions 8–10

B_2H_7 (**8**). An earlier ab initio study (including MP2/6-31G* geometry optimizations)[39] showed the $B_2H_7^-$ anion to be strongly bent as has been found in the solid state.[40,41] The symmetrical C_2 form **8c** turned out to be the minimum, whereas the slightly unsymmetrical C_s form **8b** has one imaginary frequency and therefore should be a transition state (the linear D_{3d} structure has two imaginary frequencies denoting a "hilltop"). As in the case of B_4H_{10} (see above), optimization of **8a** and **8b** at the MP2/6-31G** level does not affect structure and nature of these forms significantly.

In the solid state, however, C_s symmetry with an unsymmetrical B–H–B bridge is found.[40,41] According to the calculations, the potential energy surface is very flat; e.g., the BH_3 groups can rotate nearly without a barrier. Hence, crystal packing forces may well dominate the actual geometry in the solid state. In the gas phase or in solution more symmetric forms are to be expected.

The crucial geometric parameter that governs the chemical shifts of $B_2H_7^-$ seems to be the B–H–B angle. The level of theory employed in the optimization strongly affects the value of this angle; the inclusion of electron correlation is especially important[39] (e.g., for **8c** the B–H–B angle is 140.8° at 6-31G* and 126.4° at MP2/6-31G*). The significant ^{11}B chemical shift differences between the 6-31G* and the MP2/6-31G* geometries for **8b** and **8c** show optimizations with correlation to be essential here. The IGLO ^{11}B chemical shifts of the bent forms **8b** and **8c**, −22.9 and −23.1 ppm, respectively, are in close agreement with the experimental value (−24.6 ppm).[42] Since linear **8a** shows a significant deviation (−14.7 ppm), the bent B–H–B moiety found in the solid state obviously is retained in solution. However, since the chemical shifts of **8b** and **8c** are nearly identical, no distinction between these two forms can be made on this basis.

The imperfections of the X-ray structure with respect to the hydrogen locations are shown by an IGLO calculation employing this geometry, which results in poor agreement with the experimental chemical shifts (Table II). On the other hand, the IGLO values based on the structure derived by neutron diffraction are

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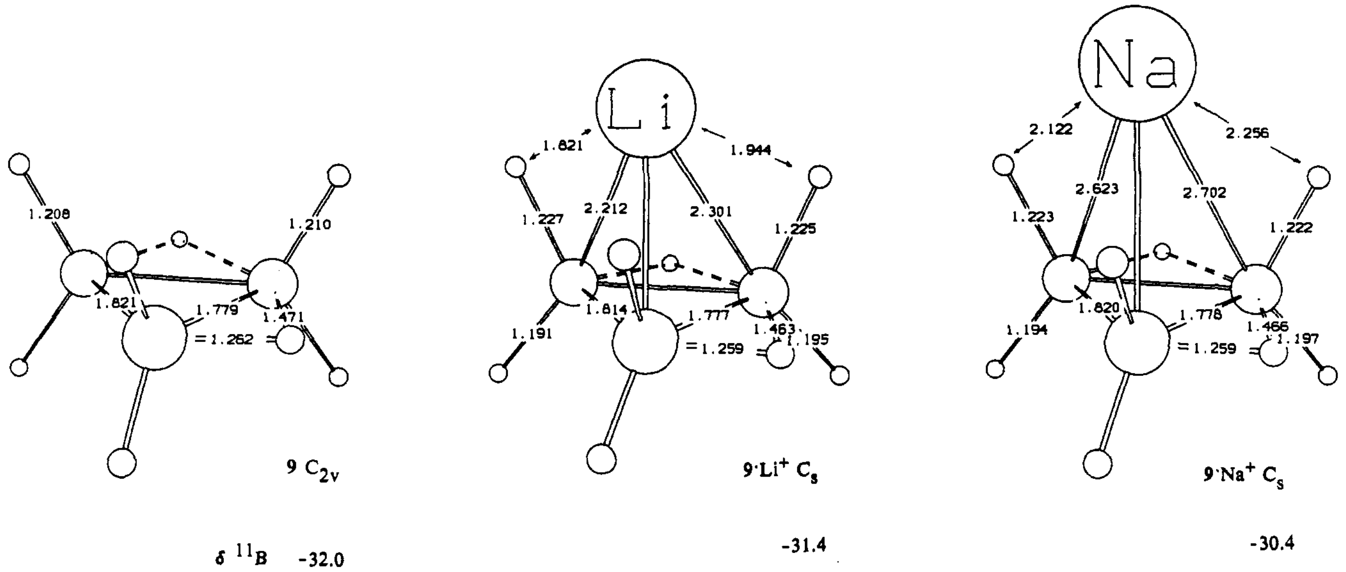

Figure 4. Comparison of geometries (MP2/6-31G* optimized) and averaged ^{11}B chemical shifts (IGLO II′//MP2/6-31G*) for $B_3H_8^-$ (**9b**), B_3H_8Li, and B_3H_8Na.

in good accord with experiment.

$B_3H_8^-$ (9). Of the two structural alternatives considered, **9a** with C_s with **9b** with C_{2v} symmetry, the latter has been found in crystal structures.[43] McKee and Lipscomb[44] have examined the relative energies of **9a** and **9b** at various levels of theory, but only with 3-21G optimized geometries. Reoptimization at 6-31G* and MP2/6-31G* affords somewhat shorter bond distances. The MP2 geometry is in good agreement with the X-ray structures.

The nature of the two stationary points depends on the level of theory employed: At Hartree–Fock levels (3-21G, 6-31G*), **9a** is a minimum and is lower in energy than **9b** (transition state), whereas this is reversed at MP2/6-31G*: at this correlated level, **9b** is a minimum and **9a** a transition state. The very low scrambling barrier, ca. 0.9 kcal/mol,[10,44] is consistent with the fluxional character of the molecule.

The averaged IGLO chemical shifts (DZ//MP2/6-31G*) are in good accord with experiment for **9b** (−31.6 ppm, exptl: −29.8) but show a significant deviation for **9a** (−21.1 ppm). This indicates the C_{2v} form of the solid state to be present in solution as well. The individual chemical shifts of the static form **9a** (−50.6, −7.5 ppm, basis II′) are comparable to those found experimentally for B_3H_7L Lewis base adducts which possess C_s symmetry (e.g., −52.6, −6.4 ppm for L = CO;[47] −51.6, −11.2 ppm for L = PH_3[48]).

The rather good agreement of chemical shifts computed for isolated neutral boranes with measured values for the species in solution (see Table II) suggests that solvent effects on the chemical shift usually play only a minor role. But is this also true for the effects of counterions in the case of the anionic boron hydrides? To clarify this point, we studied the complexes of **9** with Li^+ and Na^+. The MP2/6-31G* optimized geometries in Figure 4 demonstrate that the key geometric parameters of **9** remain practically unchanged. Although the overall molecular symmetry is reduced to C_s in the complexes, the bridging hydrogens remain in the BBB plane. As it is the case with the geometries, the calculated (averaged) chemical shifts of **9**, **9**·Li^+, and **9**·Na^+ show only minor differences. This is also found experimentally for many different counterions.[49] Hence, the chemical shifts of anionic boron hydrides should be described reasonably well by regarding the "naked" anions.

$B_4H_9^-$ (10). No X-ray structure is known for a $B_4H_9^-$ salt. On the basis of the NMR spectrum,[50] a C_s symmetric structure (**10**) with "fractional three-center BBB bonds"[51] has been proposed.

We carried out geometry optimizations in C_s symmetry including polarization functions and electron correlation; a frequency calculation showed this structure to be a minimum at the 6-31G* level. As pointed out above, the structural parameters for $B_4H_9^-$ optimized at the MP2/6-31G* level should be reliable. This is confirmed by the IGLO results for **10** which are in excellent agreement with the experimental chemical shifts.

Carboranes 11–21

1,3-$C_2B_2H_4$ (11). Although a search for this smallest conceivable *closo*-carborane has been undertaken by a number of chemists, the parent compound is still unknown. A rather open, puckered four-membered ring structure rather than a closo-type "tetrahedron" has been predicted.[52] A number of substituted derivatives has been synthesized, and some of them characterized by X-ray structure analysis. For these, the puckered C_2B_2 unit has been confirmed.[53,54]

More refined geometric parameters and the predicted chemical shifts for the parent compound **11** are included in Tables I and II. A discussion of substituent effects on δ ^{13}C in this system will be published elsewhere.[54]

1,5-$C_2B_3H_5$ (12). The structure of this smallest known *closo*-carborane has been determined by electron diffraction.[55] The MP2/6-31G* optimized geometric parameters for **12** (D_{3h} symmetry) are in good agreement with the experimental results (Table I). A frequency calculation at the correlated MP2/6-31G* level confirmed this D_{3h} form to be a minimum.

As mentioned above, the IGLO δ ^{11}B chemical shifts for **12** give only poor accord with experiment (Table II). Employing the

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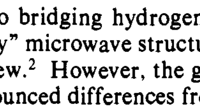
GED structure results in a deviation of ca. 12 ppm. The 3-21G and 6-31G* geometries perform even worse (19 and 15 ppm deviation, respectively), and at the highest level of theory, II′//MP2/6-31G*, the boron is computed too strongly deshielded by 10 ppm. A GIAO calculation (6-31G* basis set) employing the MP2/6-31G* geometry gives essentially the same result.[56] This suggests that the basic theoretical procedure underlying the chemical shift calculations (which remains at Hartree–Fock level, i.e., without treatment of electron correlation) may not be sufficient in this case.

The dependence of the calculated chemical shifts on the geometric parameters is not very pronounced: if one artificially reduces the BB distance in the MP2/6-31G* geometry of **12** from 1.853 to 1.750 (leaving the BC distance constant), then the computed δ ^{11}B value of 5.3 ppm is closer to the experimental value (1.4 ppm). However, this geometry is not realistic: the distortion "costs" 14 kcal/mol. The reason for the discrepancy between theoretic and experimental chemical shifts in this case is not known. Perhaps a correlated wave function is needed for the chemical shift calculation.

1,2-$C_2B_3H_7$ (13). This relatively unstable *nido*-carborane—which instantaneously polymerizes in the liquid state—is isoelectronic with B_5H_9 (**3**). Since three-center C–H–B bridges usually are avoided, one carbon atom assumes an apical position to accomodate the two bridging hydrogens. A previously unpublished, "preliminary" microwave structure has been reported by Beaudet in his review.[2] However, the geometric parameters given there show pronounced differences from those obtained by ab initio optimizations (Table I). The computed and the experimental bond distances differ by up to 0.19 Å. E.g., the reported short CC distance of 1.453 Å is not reproduced by the calculations (MP2/6-31G*: 1.604 Å).

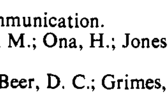
As mentioned above, the IGLO ^{11}B chemical shifts for **13** do not agree with the experimental values. The maximum deviation is ca. 19 ppm for the microwave structure and ca. 9 ppm for the MP2/6-31G* geometry (DZ basis). Even at the highest theoretical level employed, II′//MP2/6-31G*, computed and experimental chemical shifts differ by ca. 8 ppm (Table II). Together with δ ^{11}B of 1,5-$C_2B_3H_5$ (**12**), these deviations are considerably larger than found for the other molecules of this study (cf. Table III). Evidently, small strained carboranes **12** and **13** require even higher (e.g., correlated) levels of theory for a correct description of geometries and chemical shifts.

The computed large upfield shift for the apical carbon C1 in **13** (−34.8 ppm at the II′//MP2/6-31G* level) compares rather well to the value of −23.0 ppm reported for C1 in Masamunes's cation, a substituted derivative of the isoelectronic $(CH)_5{}^+$.[57]



The δ ^{13}C chemical shifts computed for **13** are strongly dependent on the basis set used in the IGLO calculation (Table II). Unfortunately, no experimental data are known for comparison.

We also considered a cyclic isomer of **13** (C_s symmetry), which—in reduced form—can act as a ligand in transition-metal complexes.[58] However, at the MP2/6-31G*//MP2/6-31G* + ZPE(6-31G*) level this isomer is less stable than **13** by 16.6 kcal/mol.



1-CB_5H_7 (14). The molecular structure of CB_5H_7 (**14**) has been the topic of several experimental[59] and theoretical[29] studies. While there is general agreement that the carborane cage consists of a distorted octahedron, the exact position of the "extra" hydrogen has been the matter of some debate. In the GED study,[59a] this hydrogen was reported to bridge the B(2)B(3)B(6) face; however, the electron diffraction technique is less reliable when two or more bond distances of the same magnitude are involved. In the MW study,[59b] no hydrogens were refined at all. The three somewhat elongated B–B distances on one of the cage faces strongly favored the triply bridging arrangement. In the Beaudet's recommended structure, a position for the critical H with three nearly identical B–H lengths was assumed. In contrast, ab initio calculations at the 3-21G level showed a very unsymmetric arrangement (with respect to the triangular face), the three B–H distances being 1.353, 1.353, and 1.857 (!) Å, respectively (Table I).[29] At the highest level employed, MP2/6-31G*, the calculated dimensions of the carborane cage agree well with those inferred from experiment. The critical hydrogen exhibits the most dramatic sensitivity toward the theoretical level: the nature of this bridge changes from an essentially three-center bond at 3-21G to a nearly pure four-center bond at MP2/6-31G* (B–H distances 1.389, 1.389, 1.475 Å). The 6-31G* geometry is intermediate between these two. This sensitivity toward the computational level is indicative of a very flat potential energy surface for the motion of the critical hydrogen.

The IGLO results for CB_5H_7 (Table II) show a pronounced dependence on the various geometries employed. The most sensitive atom, B6, is involved in the critical hydrogen bridge. As the B6–Hb distance decreases in going from the 3-21G to the MP2/6-31G* geometry this boron is increasingly shielded. At the highest theoretical level employed (II′//MP2/6-31G*), the agreement between theoretical and experimental δ ^{11}B values is excellent.

More refined calculations on the transition structure and the barrier for hydrogen scrambling in CB_5H_7 will be reported elsewhere.[60]

1,2-$C_2B_4H_6$ (15) and 1,6-$C_2B_4H_6$ (16). There is no unusual dependence of computed geometries and chemical shifts on the level of theory for these two *closo*-carborane isomers. The 1,6-isomer, **16**, is more stable than **15** by 9.7 kcal/mol at MP2/6-31G*//MP2/6-31G* + ZPE(6-31G*). This value is in agreement with calculations reported by McKee (employing 3-21G geometries)[61] who also investigated the reaction path interconverting the two isomers. Electron-releasing amino substituents on boron favor a bicyclic, "classical" isomer.[62]

2-CB_5H_9 (17), 2,3-$C_2B_4H_8$ (18), 2,3,4-$C_3B_3H_7$ (19), and 2,3,4,5-$C_4B_2H_6$ (20). These four *nido*-carboranes are structurally related to B_6H_{10}; they are derived formally by successive replacement of one boron and one bridging hydrogen by a carbon. All have the same basic pentagonal-pyramidal structure (Figure 2).

For 2-CB_5H_9 (**17**), a partial microwave structure was published,[63] without refinement of carbon and hydrogen positions. The reported B–B distances are in good agreement with the computed values (Table I). Beaudet tabulated coordinates for all atoms in his review, probably based on reasonable assumptions. The IGLO ^{11}B chemical shifts for his recommended structure, however, show a large deviation for B1 (−38.7 ppm, exptl: −51.9, Table II). The IGLO values computed for the ab initio geometries are in good accord with experiment, without even showing large dependence on the level of theory. The same is found for 2,3-$C_2B_4H_8$ (**18**).

For 2,3,4-$C_3B_3H_7$ (**19**), neither an accurate structure nor chemical shifts are known experimentally. Substituted derivatives

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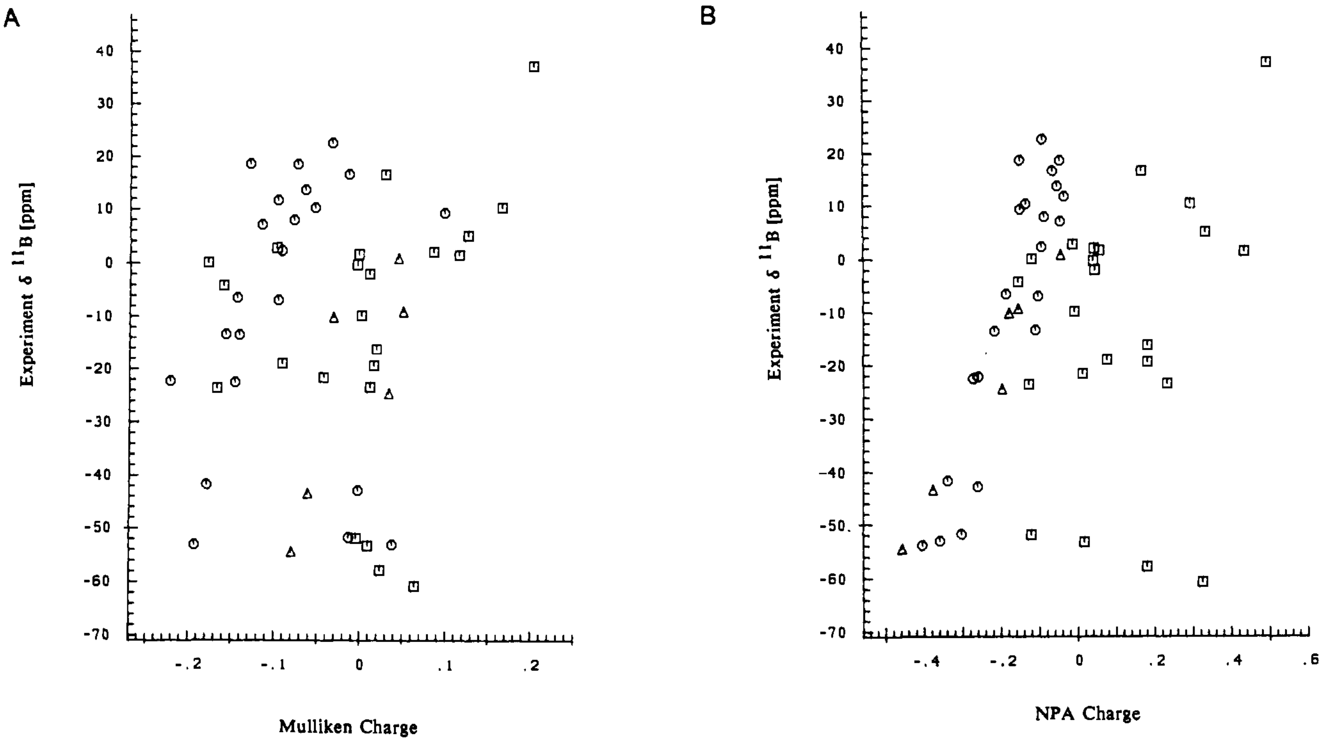

Figure 5. Correlation of ^{11}B chemical shifts with atomic charges obtained (a) from Mulliken and (b) from natural population analysis (NPA): circles, neutral boranes **1–7**; triangles; borane anions **8–10**; squares, carboranes **11–21**.

have been prepared. The chemical shift of B1 measured for 2,4-dimethyl-2,3,4-$C_3B_3H_5$, −51.6 ppm,[64] differs somewhat from that computed for the parent compound **19**, −57.9 ppm. The latter value, however, is in line with the trend observed in **17–20**: an increasing number of basal carbon atoms is paralleled by a high field shift of B(1): −51.9, −53.3, −57.9 (IGLO) and −60.8 ppm for **17**, **18**, **19**, and **20**, respectively (see Table II).

The MP2/6-31G* optimized geometrical parameters of 2,3,4,5-$C_4B_2H_6$ (**20**) are very similar to the reported 6-31G* values[65] and are in good accord with the microwave data. The IGLO ^{11}B chemical shifts also agree well with experiment.

2,4-$C_2B_5H_7$ (21). The structure of **21**, the largest carborane included in this study, has been determined by MW[66] and by GED,[67] where the molecular C_{2v} symmetry was established. Although the computed structural parameters depend somewhat on the level of theory (Table I), the ^{11}B IGLO DZ chemical shifts show only minor differences for the various ab initio geometries (ca. 2 ppm, Table II). The effect of the larger II′ basis set with respect to the DZ basis is more pronounced: the computed δ ^{11}B values differ up to ca. 4 ppm (compare DZ//MP2/6-31G* and II′//MP2/6-31G* values in Table II). However, the ^{11}B chemical shifts calculated at the highest level (II′//MP2/6-31G*) agree rather well with the experimental values (maximum deviation ca. 3 ppm).

^{13}C Chemical Shifts. Experimental ^{13}C data for the unsubstituted small carboranes are very sparse.[68] Among the compounds of this study, only δ ^{13}C values for 1,3-$C_2B_3H_5$ (**12**), 1,6-$C_2B_4H_6$ (**16**), 2,3-$C_2B_4H_8$ (**18**), and 2,4-$C_2B_5H_7$ (**21**) have been published.[68] The IGLO chemical shifts of these four compounds (II′//MP2/6-31G* level, Table II) are in moderately good agreement with the literature data; the largest deviation is ca. 7 ppm for **16**.

Two general characteristics are observed for the computed δ ^{13}C values: First, the IGLO ^{13}C chemical shifts usually are not very sensitive to small geometric changes (DZ values, Table II). In many cases, the variation in δ ^{11}B is larger. Second, larger IGLO basis sets sometimes strongly affect the computed δ ^{13}C values (compare DZ//MP2/6-31G* and II′//MP2/6-31G* values in Table II). In some systems, the DZ − II′ difference can be rather large (e.g., up to 15 ppm in **13**). The II′ δ ^{13}C values usually are shifted upfield with respect to the DZ results (except **12** and **21**). Interestingly, the IGLO δ ^{13}C values are too far upfield with respect to available experimental data. A critical evaluation of these deviations, however, must await more experimental determinations. Consequently, only qualitative trends can be discussed. Most of the ^{13}C chemical shifts calculated for **12–21** are in the range between ca. 80 and 120 ppm. Interesting exceptions are the resonances at higher field predicted for 1-CB_5H_7 and 1,2-$C_2B_4H_6$ (around ca. 45 ppm) and, as mentioned above, C1 of 1,2-$C_2B_3H_7$ (ca. −30 ppm).

Discussion

The most obvious property with which the chemical shift might be correlated is the atomic charge. Several correlations of δ^{11}B with total or π charge densities have been reported.[69,70] The atomic charges—which are not observable properties—mostly were calculated at semiempirical levels employing Mulliken population analysis (MPA).

We employed another method, natural population analysis (NPA)[71] which generally has the advantage of showing little basis set dependence. The results of these two methods (6-31G* basis set for MP2/6-31G* geometries) are compared in Table V and are correlated with the experimental chemical shifts[72] in Figure 5.

The NPA charges span a considerably wider range than those obtained from Mulliken analysis, and it may seem to be unusual

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for a boron to bear nearly half a negative (B1 in $B_4H_9^-$, **10**) or half a positive charge (in 1,5-$C_2B_3H_5$, **12**). The plots in Figure 5 illustrate that there is no general relationship between ^{11}B chemical shifts and total atomic charges. While one might perceive a trend for the binary boron hydrides in the plot vs NPA charges (○ and Δ in Figure 5b), this is not found at all for the carboranes (□). Boron atoms attached to the more electronegative carbon appear to be more positively charged. However, this is not reflected in the ^{11}B chemical shifts.

The apical borons B1 in the series of pentagonal pyramids **17**–**20** (the □ in lower half of Figure 5b) are unique in showing exceptionally strong upfield shifts with respect to the computed charges. This might support the ring current models that have been proposed to explain proton NMR chemical shifts of substituted compounds.[73]

Conclusions

The ^{11}B chemical shifts of several boron hydrides and carboranes have been calculated ab initio using the IGLO method. Except for the two smallest carboranes, the agreement between theoretical and experimental values is excellent provided accurate geometries are employed (e.g., optimized ab initio with inclusion of electron correlation). A correct description of δ ^{11}B chemical shifts in carboranes is somewhat more demanding with respect to the level of theory employed: in many cases, the larger TZP type basis II′ is needed in order to reproduce the experimental results. The accuracy that can be achieved is remarkable: although two of the observed boron resonances of B_8H_{12} differ by merely 2 ppm, an alternative assignment is suggested by the IGLO calculations.

The effect of counterions on geometry and chemical shifts is shown to be very small in the case of $B_3H_8^-$. Hence, even the treatment of anions as isolated molecules seems justified, and no inherent errors are apparent.

A pessimistic opinion states only two years ago, "...theoretical calculations of these NMR characteristics are of little importance because they cannot be performed as accurately as necessary for the structural elucidation of boron compounds"[38] no longer is valid. A certain limitation, however, is that this accuracy—at least in the case of polyhedral boranes—can only be achieved for geometries optimized at a correlated level (these optimizations can be rather expensive, e.g., 50 000 CPU s for the MP2/6-31G* optimization of B_6H_{12} on a CRAY-YMP).

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Registry No. **1**, 19287-45-7; **2**, 18283-29-9; **3**, 19624-22-7; **4**, 18433-84-6; **5**, 23777-80-2; **6**, 12008-19-4; **7a**, 19469-16-0; **8a**, 27380-11-6; **9a**, 12429-74-2; **10**, 12429-85-5; **11**, 90171-84-9; **12**, 20693-66-7; **13**, 26249-71-8; **14**, 55188-36-8; **15**, 20693-67-8; **16**, 20693-68-9; **17**, 12385-35-2; **18**, 18972-20-8; **19**, 12403-04-2; **20**, 28323-17-3; **21**, 20693-69-0.

Supplementary Material Available: Cartesian coordinates of the MP2/6-31G* optimized structures of **1**–**21** (7 pages). Ordering information is given on any current masthead page.

The Structural Variations of Monomeric Alkaline Earth MX_2 Compounds (M = Ca, Sr, Ba; X = Li, BeH, BH_2, CH_3, NH_2, OH, F). An ab Initio Pseudopotential Study

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Abstract: The geometries of a series of monomeric alkaline earth MX_2 compounds (M = Ca, Sr, Ba; X = Li, BeH, BH_2, CH_3, NH_2, OH, F) have been calculated at the Hartree–Fock level, using quasirelativistic pseudopotentials for Ca, Sr, and Ba. The energies of fully optimized structures are compared with those of linear X–M–X geometries. Most barium compounds studied (except $BaLi_2$) are bent with angles between 115 and 130° and linearization energies up to ca. 8 kcal/mol (for $Ba(CH_3)_2$). The degree of bending for M = Sr is smaller but is still significant (except for X = Li, BeH). However, most of the Ca compounds may be termed quasilinear, i.e., they either are linear or nearly so and bend easily. The XMX bond angles for M = Sr, Ba do not decrease monotonously along the series X = Li, BeH, BH_2, CH_3, NH_2, OH, F but show a minimum for X = CH_3! Natural atomic orbital population analyses indicate the larger angles with O, N, and F to be due to π-type interactions of lone pairs with empty metal d-orbitals. These $p_\pi \rightarrow d_\pi$ interactions tend to favor linear structures. For the diamides (X = NH_2), significant π-bonding contributions lead to a preference for C_{2v} structures with the hydrogen atoms in the N–M–N plane over C_s or out-of-plane C_{2v} geometries. The barriers to rotation around the M–N bonds are significant. For X = BH_2, C_s and out-of-plane C_{2v} arrangements are slightly more favorable than an in-plane C_{2v} geometry. The dimethyl compounds generally exhibit almost free MCH_3 rotation.

Introduction

Inorganic chemistry textbooks usually treat the chemistry of Ca, Sr, and Ba (e.g., the bioinorganic chemistry of Ca) as that of completely ionic systems, neglecting covalent bonding contributions or even any deviations from a rigid spherical dication model. These assumptions may well be justified in some respects. However, the bent structures of some monomeric dihalides of the heavier group 2 elements are major exceptions to the valence shell electron pair repulsion (VSEPR) model.[1] This is also true for all other common structural models for main group chemistry,[2] including those based only on coulombic forces, assuming completely ionic bonding. There is continuing experimental and

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