Even More Reliable NMR Chemical Shift Computations by the GIAO-MP2 Method

Paul von R. Schleyer,*[a] **Jürgen Gauss,**[b] **Michael Bühl,**[c] **Robert Greatrex***[d] **and Mark A. Fox**[d]

[a] *Institut für Organische Chemie, Universität Erlangen-Nürnberg, D-91054 Erlangen, Germany*
[b] *Lehrstuhl für Theoretische Chemie, Institut für Physikalische Chemie, Universität Karlsruhe, D-76128 Karlsruhe, Germany*
[c] *Center of Computational Quantum Chemistry, University of Georgia, Athens, GA 30602 USA*
[d] *School of Chemistry, University of Leeds, Leeds, UK LS2 9JT*

Correlated *ab initio* (GIAO-MP2) chemical shift computations agree excellently with the newly remeasured ^{11}B and ^{13}C NMR values for the problem carboranes, **1** and **2**, which had given poor IGLO results.

Structural assignments based on the *ab initio*/IGLO/NMR method[1] are quickly approaching a confidence level that rivals modern-day X-ray determinations of molecular structures.[2] An important basis for this remarkable assessment was provided by a systematic investigation of the performance of ^{11}B IGLO chemical shift computations on a set of 21 boranes and carboranes.[3] The IGLO values calculated using Beaudet's recommended experimental geometries, based on carefully evaluated MW, GED and X-ray data,[4] were inferior, in comparison with experimental $\delta^{11}B$s, to the IGLO values obtained using the MP2/6-31G* optimized geometries.[3,5] At the highest level employed (IGLO II′//MP2/6-31G*),[1b] the standard deviation in $\delta^{11}B$ *vs.* experiment was 3.1 ppm for all 21 compounds. The largest deviations were 10 ppm for 1,5-$C_2B_3H_5$ **1** and 8 ppm for both types of boron atoms in 1,2-$C_2B_3H_7$ **2**. This paper concerns these 'problem' molecules. When these were removed from the set, the standard and largest deviations were reduced to only 1.3 and 3.1 ppm, respectively.[3]

Experience suggests[3] that the disagreements between theory and experiment for **1** and **2** may have three origins. (*a*) Errors inherent in the computations of chemical shifts, or (*b*) errors in the experimental chemical shift measurements, or (*c*) inaccuracies in the geometries employed for the chemical shift computations.

Indeed (*c*) forms the basis for the combined *ab initio*/IGLO/NMR method of structural determination,[1] where the best candidate geometry is selected on the basis of the degree of agreement between the computed and the experimental chemical shifts.

The reliability of any method depends not only on its average performance, but also on the lack of exceptions. Are **1** and **2** really exceptions when applying the IGLO method? If so, is it possible to improve the results? The newly-developed GIAO-MP2 method[6] allows electron correlated chemical shifts to be computed routinely for the first time. In general, GIAO-SCF[7] gives results that are comparable to IGLO (an SCF method).[1b] In molecules where both these SCF methods perform well, the GIAO-MP2 results are at least as good (*e.g.* on boron chemical shifts).[8c] However, in cases where the SCF methods perform poorly, decisive improvement has been achieved with GIAO-MP2 (*i.e.* by inclusion of electron correlation).[6b,8] Does GIAO-MP2 improve the SCF (IGLO and GIAO) performance on **1** and **2**?

1,5-$C_2B_3H_5$ **1**. The 10.0 ppm $\delta^{11}B$ IGLO error is compounded by a $\delta^{13}C$ discrepancy of 5.8 ppm. The experimental and computed geometries agree well, as do the several determinations of the chemical shifts. We suggested that the basic theoretical procedure underlying the chemical shift calculations (which remains at the Hartree–Fock level, *i.e.* without treatment of electron correlation) may not be sufficient in this case.[3] This is now shown to be correct.

The new GIAO-MP2 method,[6] which includes dynamic electron correlation in chemical shift computations, gives greatly improved results with **1** (Table 1). With a TZP/DZP(H) basis set (TZP′) and the MP2/6-31G* geometries, the computed $\delta^{11}B$ 1.9 is within 0.5 ppm of the older, and within 1.6 ppm of the new experimental values. The $\delta^{13}C$ discrepancy is only 0.9 ppm! The accompanying computation at the SCF level (GIAO-SCF) gives errors for **1** (see Table 1), which are comparable to the IGLO results (also at SCF). The influence of electron correlation on $\delta^{11}B$ for **1** is exceptional. This is the only compound among the 21 considered which can be described formally by a classical representation (tricoordinate boron and tetracoordinate carbon atoms); however, the true electronic structure is highly delocalized.

1,2-$C_2B_3H_7$ **2**. This unstable compound has not been investigated as extensively as **1**. The reported ^{11}B chemical shifts for both boron atoms differed from the best IGLO values by 8 ppm (see Table 2); the $\delta^{13}C$s were not determined in the original work.[9] The proposed structure of **2** is consistent with the bonding preferences of carbaboranes and was supported by IR as well as NMR spectroscopic data. The bridging Hs involve boron atoms, requiring one of the carbon atoms to adopt a high-coordination site. A preliminary MW structure has been mentioned,[4] but this did not agree at all with the *ab initio* geometries.[3]

We expended considerable effort in searching for alternative $C_2B_3H_7$ minima.[3-10] Monocyclic structures similar in energy to **2** were located, but these gave computed chemical shifts which were far from the experimental values. In contrast, the computed IR spectra of **2** [both at HF/6-31G*

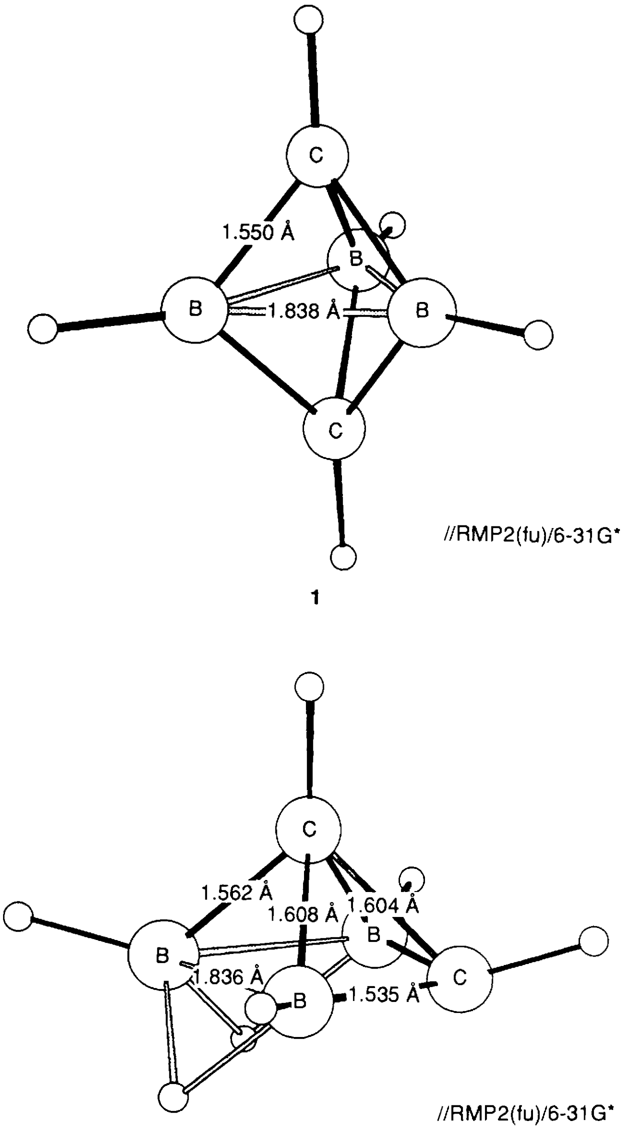

Fig. 1

Table 1 Experimental and computed ^{11}B and ^{13}C chemical shifts

1,5-$C_2B_3H_5$ **1**	C(1,5)	B(2,3,4)
Expt.[a]	103.3[a]	1.4[a] 3.5[b]
IGLO-SCF/II′ (1992)[a]	97.5	11.4
GIAO-SCF/TZP′	95.4	11.8
GIAO-MP2/TZP′	104.2	1.9
Difference MP2 *vs.* expt.	+0.9	−1.6

[a] See ref. 3. [b] This work.

Table 2 Experimental and computed ^{11}B and ^{13}C chemical shifts

1,2-$C_2B_3H_7$ **2**	C(1)	C(2)	B(3,5)	B(4)
Expt. 1972[a]	—	—	−21.7	−23.7
Expt. 1993[b]	−21.5	57.9	−13.39	−15.07
IGLO-SCF/II′ (1992)	−34.8	48.6	−13.6	−15.7
GIAO-SCF/TZP′	−30.5	51.7	−13.3	−14.7
GIAO-MP2/TZP′	−23.1	57.4	−14.6	−16.0
Difference MP2 *vs.* expt. 1993	−1.6	−0.5	−1.2	−0.9

[a] Ref. 9. [b] This work.

and at MP2(fc)/6-31G*], agree excellently with the reported gas-phase spectrum.[9b] Hence, possibility (*c*) is eliminated: the computed (but not the preliminary MW) structure of **2** appears to be correct.

What about possibility (*a*)? Initially, the GIAO-MP2 results (see Table 1) seemed disappointing. There was no significant improvement in the $\delta^{11}B$ values from the earlier IGLO results.[3] While correlation effects were noted on the computed $\delta^{13}C$ values (Table 1), experimental data were not available.

What about possibility (*b*)? Measurements of $\delta^{11}B$ were not nearly as straightforward in the early 1970s as they are today ($\delta^{13}C$ determinations are still complicated by quadrupole broading due to adjacent boron atoms). Repetition of the preparation of **2** at Leeds has now led to the new NMR data summarized in Table 2. The 1992 $\delta^{11}B$ IGLO predictions[3] were almost exactly correct after all! The average error is only 0.4 ppm based on the new NMR data. Evidently, the scale of the earlier experimental values had been displaced inadvertently by *ca.* 8.5 ppm.

As for unsaturated organic molecules[6b] and ions,[8a,b,d] GIAO-MP2 proves its superiority over the SCF methods in the $\delta^{13}C$ predictions for **2**. The average GIAO-MP2 discrepancy is only 1.1 ppm (Table 1), in contrast to 11.3 ppm for IGLO[3] and 7.6 for GIAO-SCF.

The determination of the accurate molecular geometries of boron compounds, with their interlocking skeletal bonding and bridging hydrogen arrangements, has been among the most challenging structural problems.[4] Modern theoretical methods are now able not only to provide these geometries reliably but also to compute ^{11}B chemical shifts which agree to 1–2 ppm with experiment. Even modest SCF theoretical geometries as well as SCF chemical shift computations (IGLO and GIAO-SCF) often give quite acceptable agreement with experimental NMR measurements.[1–3] However, the more accurate electron correlated (*e.g.* MP2/6-31G*) geometries generally give superior results[3] and chemical shifts computed at GIAO-MP2 are needed for the more demanding boron cases, and especially for the accurate computation of ^{13}C shifts.[6b,8]

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