arachno-2-Gallatetraborane(10), $H_2GaB_3H_8$: An *Ab initio* Molecular Quantum Mechanical Study

Brian J. Duke[a,b] **and Henry F. Schaefer III**[a]

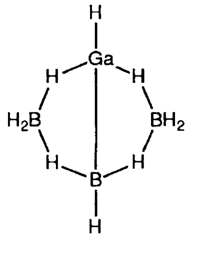
[a] *Center for Computational Quantum Chemistry, University of Georgia, Athens, GA 30602, USA*
[b] *School of Chemistry and Earth Sciences, Northern Territory University, PO Box 40146, Casuarina, NT 0811, Australia*

The isomers *arachno*-2-gallatetraborane(10) and *arachno*-1-gallatetraborane(10) have been studied by *ab initio* molecular quantum mechanical methods, following the synthesis of the 2-derivative by Downs and coworkers; substantial basis sets, *e.g.* Ga (14s 11p 6d/7s 5p 3d), have been used in conjunction with the self-consistent-field approximation and both structures are genuine minima, the terminal gallium structure being predicted to lie lower than its isomer by 24 kcal mol^{-1} (1 cal = 4.184 J).

The chemistry of gallium compounds containing bridging hydrogen atoms similar to the boranes has recently expanded. Digallane,[1] its tetramethyl derivative[2] and gallaborane ($H_2GaH_2BH_2$)[3] have been synthesised and structures determined. Theoretical studies have been made on digallane[4–5] and gallaborane.[7] Pulham *et al.*[8] have recently synthesised and made electron diffraction measurements on the gallatetraborane(10), 2-$H_2GaB_3H_8$, and found it to be appreciably more robust than either digallane or gallaborane. The dimethyl derivative 2-$Me_2GaB_3H_8$ and the related aluminium compound 2-$Me_2AlB_3H_8$ were characterised earlier.[9,10] Many other metallaborane structures have been synthesised (see review by Kennedy[11]).

We report *ab initio* molecular orbital studies of 2-$H_2GaB_3H_8$ along with the unknown 1-$H_2GaB_3H_8$. The two isomers, *arachno*-1- and -2-gallatetraborane(10), are shown as structures **I** and **II** respectively. An initial geometry estimation was obtained with the Huzinaga–Dunning[12,13] double-zeta basis sets for boron (9s5p/4s2p) and hydrogen (4s/2s) and the effective core potential (ECP) method and double-zeta basis of Igel-Mann *et al.*[14] for gallium (ECP-DZ, 58 basis functions). For heavy atoms this approach is an alternative to the usual preliminary survey of the potential energy hypersurface with the small STO-3G basis set. Polarisation functions were then added to all atoms, while retaining the core potential on gallium (ECP-DZP, 112 basis functions). Finally the all-electron Dunning[15] 14s 11p 5d/7s 5p 2d + polarisation (η_d = 0.16) basis was used for gallium (DZP, 132 basis functions). All calculations were carried out using the TURBOMOLE system of Ahlichs and coworkers.[16]

Table 1 gives the energy difference between the two isomers. The 2-isomer is more stable than the 1-isomer by around 24–25 kcal mol^{-1} if a DZP basis set is used, both with and without ECPs.



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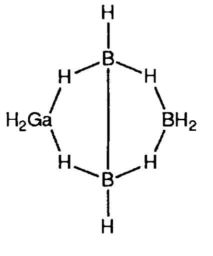

II

Table 1 Stabilisation energy of 2-gallatetraborane(10) **II** over 1-gallatetraborane(10) **I**

Method and basis set	Energy/kcal mol^{-1} [a]
ECP-DZ	20.5
ECP-DZP	25.1
All-electron DZP	24.4

[a] 1 cal = 4.184 J.

The purely *ab initio* optimised geometries using the DZP basis set are shown in Figs. 1 and 2. At the lower 3-21G* level of theory, both structures have been confirmed to be genuine minima. In 1-gallatetraborane(10) the B–H–B–H–B side of the molecule is similar to tetraborane(10) with the bridging hydrogen atoms closer to the central boron atoms than the terminal BH_2 groups. The hydrogen atoms bridged to gallium are not as expected. They are closer to the BH_2 terminal groups with a B–H distance less than the B–H_b distance in H_2Ga-(μ-H)$_2$-GaH_2.[3] The Ga–H_b distance is much longer than that in H_2Ga–(μ-H)$_2$-GaH_2, while the Ga–H_t distance is slightly shorter. The BH_2 groups are similar to those in tetraborane(10).

In the energetically lower-lying 2-gallatetraborane(10) the similarities with tetraborane(10) are much greater. The B_3 (right side of diagram **II**) fragment of the molecule is similar to one half of tetraborane(10). The B–H_t distances in bridges to both gallium and boron are similar. The Ga–H_b distance is greater than that predicted for H_2Ga–(μ-H)$_2$-GaH_2, just as the terminal B–H_t distance in tetraborane(10) is greater than that in diborane. The large Ga atom fits more easily in the terminal position than the central position, in which the Ga has to drop

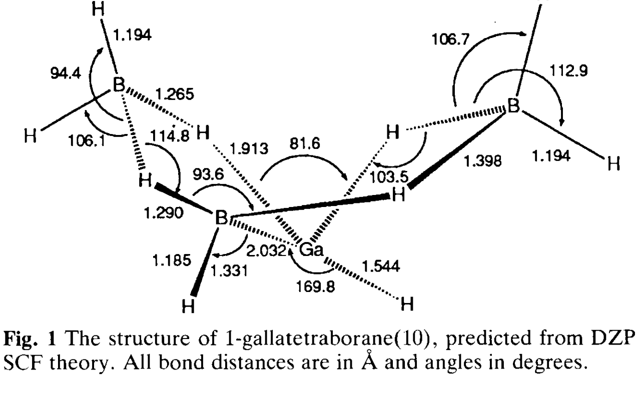

Fig. 1 The structure of 1-gallatetraborane(10), predicted from DZP SCF theory. All bond distances are in Å and angles in degrees.

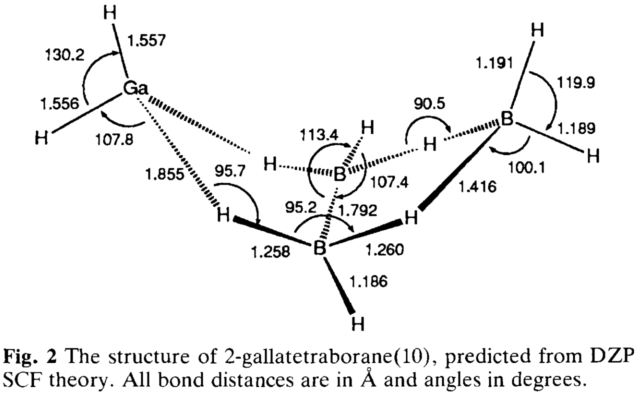

Fig. 2 The structure of 2-gallatetraborane(10), predicted from DZP SCF theory. All bond distances are in Å and angles in degrees.

well below the B atom to allow for the larger Ga–B and Ga–H distances. The B–Ga–H_t angle is almost linear. The terminal position has less steric hindrance. The large energy difference between the two isomers is thus understandable.

The Oxford group's[8] preliminary structural parameters are as follows (theoretical prediction from this work in parentheses): r[Ga–B(1)] = 2.312 (2.342) Å, r[B(1)–B(4)] = 1.842 (1.903) Å, r[Ga–H_t] = 1.445 (1.557) Å, r[Ga–H_b] = 1.783 (1.855) Å; 114.8 (117.1)° for the dihedral angle between the planes GaB(1)B(3) and B(1)B(3)B(4). The predicted bond lengths, as in previous related studies,[4–7] are longer than the experimental values. The introduction of electron correlation reduces bridge distances in other gallium–boron hydrides and would presumably do so in this case. Unfortunately, the basis set is too large and the symmetry too low for geometry optimisations with configuration interaction to be feasible at the present time. The error in the predicted distance for the terminal Ga–H bond is however surprising. It is hoped that these theoretical predictions of all bond legnths and bond angles in this molecule may assist the further analysis of the experimental data.

The predicted IR frequencies, which were only determined with the 3-21G* basis set, for 2-$H_2GaB_3H_8$ include a peak at 2280 cm^{-1} which is four times more intense than any other peak. It corresponds to a Ga–H_b–B stretching frequency. In contrast, for 1-$H_2GaB_3H_8$, there are several IR peaks with similar intensity predicted above 2000 cm^{-1} and one around 700 cm^{-1}.

This study suggests that it may be possible to synthesis the 1-isomer in addition to the 2-isomer. Digallium analogues of tetraborane, in particular 2,2′-digallatetraborane(10), are also suggested as likely molecules for synthesis.

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