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Communication

Bond rotamers and calculated ^{11}B-NMR chemical shifts in boron-containing cluster chemistry. Some effects in the {*nido*-7,8,10-PC_2B_8} system

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It is a pleasure to be able to dedicate this paper to Sheldon G. Shore on the occasion of his 70th birthday, in recognition of his fine contributions to several branches of chemistry over many years, particularly in the area of borane-based polyhedral cluster compounds.

Abstract

Rotamer changes about the *exo*-cluster C-phenyl bond in 7-Ph-*nido*-7,8,10-$PC_2B_8H_{10}$ have significant differential effects of up to ca. 6 ppm on the nuclear shieldings of adjacent boron atoms within the cluster. The phenomenon has some more general implications. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Boranes; DFT/GIAO structural/NMR calculations; Rotamers; ^{11}B nuclear shielding; Monoheterodicarbaborane clusters

In boron-containing cluster chemistry, structural calculations using ab initio or DFT methods, followed by IGLO or GIAO boron nuclear-shielding calculations based on these calculated structures [1–3], and thence comparison with experimentally observed ^{11}B shieldings from NMR experiments, are currently proving to be exceptionally useful in establishing molecular structures [4–9]. The technique involves the calculation of minimum-energy structures, sometimes of a variety of isomeric possibilities, and thence the calculation of the ^{11}B nuclear shielding of the individual boron atoms in these calculated structures. Close correspondence of these calculated shieldings with the observed nuclear shieldings, as measured by NMR spectroscopy, is then taken as confirmation that a particular calculated structure corresponds to the structure of the compound that generated the experimentally observed NMR spectrum.

The set of *nido*-type eleven-vertex carbaboranes, consisting of 7-R-*nido*-7,8,9-$PC_2B_8H_{10}$ (where R is Me or Ph), *nido*-7,8,11-$PC_2B_8H_{11}$, the [7,8,11-*nido*-$PC_2B_8H_{10}$]$^-$ anion and 7-Ph-7,8,10-*nido*-$PC_2B_8H_{10}$, has recently been isolated and structurally elucidated by this approach [5,9]. The energy-minimum structures and the δ(^{11}B) values were calculated at the reasonably high DFT-GIAO//B3LYP/6-31G* level, for which calculated δ(^{11}B) results that are typically within a maximum of ca. 2 ppm of observed are generally taken to be of confirmatory adequacy. There was one exception to this criterion in this otherwise consistent set. This was 7-Ph-*nido*-7,8,10-$PC_2B_8H_{10}$ (compound **1**) [9], which has an aromatic phenyl substituent on the phosphorus cluster site (Fig. 1). The other species in the set either had 'naked' phosphorus, or hydrogen, or local C_{3v} symmetric-top methylation, on this site. Although isomeric possibilities other than the {7,8,10-PC_2} configuration for this P-phenyl compound **1** were definitively excluded because of markedly different overall ^{11}B shield-

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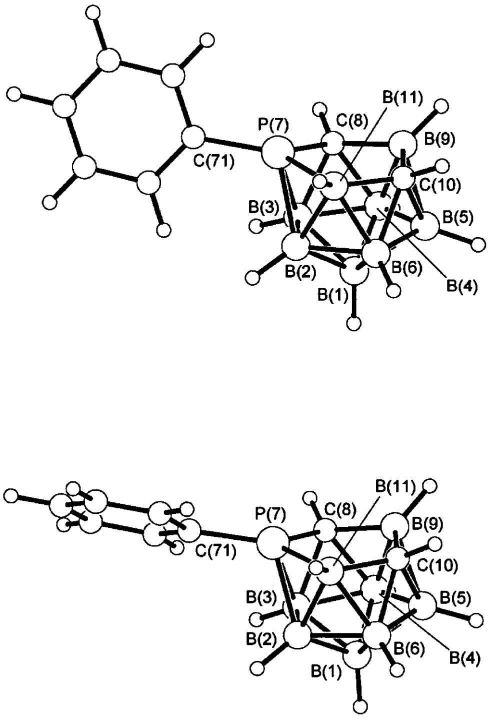

Fig. 1. General views of the DFT B3LYP/6-31G* energy/geometry-optimized structure of the higher-energy rotamer of [7-Ph-7,8,10-*nido*-$PC_2B_8H_{10}$] (**1a**) (upper diagram) and the rotamer lower energy minimum **1b** (lower diagram). Distances from P(7) for **1a** are: to C(8) 1.8558, to B(2) 2.0424, to B(3) 2.0909, to B(11) 1.9411 and to C(71) 1.8238 Å, and for rotamer **1b**: to C(8) 1.8400, to B(2) 2.0507, to B(3) 2.0832, to B(11) 1.9260 and to C(71) 1.8188 Å.

ing patterns, two of the calculated resonances, anomalously, were outside the 2 ppm limit. These were for B(1), calculated at − 37.6 ppm, some 2.1 ppm less shielded than the observed value, perhaps not remarkable, but, more dramatically, B(11), calculated at − 8.4 ppm, was now some 4.3 ppm less shielded than observed. These observed and calculated values from Ref. [9] are given in Table 1, as well as the results from the presently reported additional calculations.[1]

In our initial report on these compounds [9], we surmised that this anomaly for 7-Ph-*nido*-7,8,10-$PC_2B_8H_{10}$ (compound **1**) might be due to rotamer effects involving the P-phenyl bond, but we were then not in a position to perform the more extensive necessary calculations to test this. We have subsequently built a more rapid computational system[1] and can now report the results of further DFT-GIAO//B3LYP/6-31G* calculational investigations that confirm that there is in fact a rotamer effect. This leads to a more exact agreement between observed and calculated ^{11}B shieldings for compound **1**, and has possible wider implications.

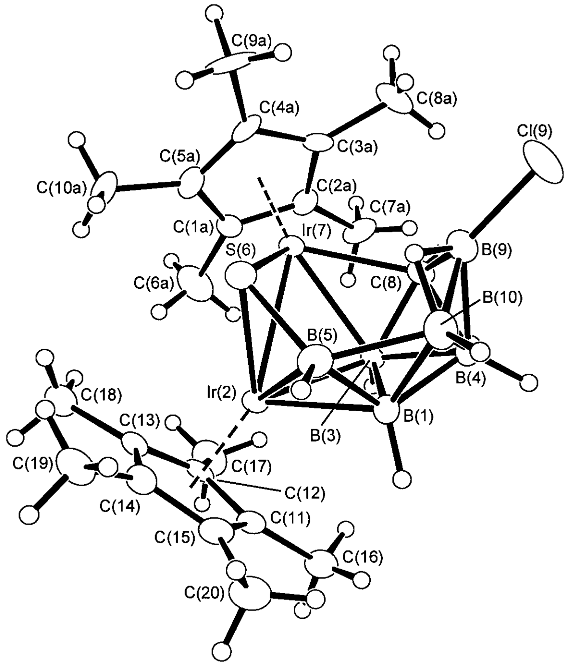

Fig. 2. Views, approximately along the P(7)–C(71) rotamer axis, of the DFT B3LYP/6-31G* energy/geometry-optimized structures for the two minima associated with contrarotation about the P(cluster)–C(phenyl) linkage of [7-Ph-7,8,10-*nido*-$PC_2B_8H_{10}$]: (top) rotamer **1a** (energy arbitrarily at zero kJ mol^{-1}), and (bottom) the more stable of the two **1b** (energy at − 3.4 kJ mol^{-1} relative to **1a**). The dihedral angles C(71)–C(72)/P(7)–C(8) for **1a** and **1b** differ by 47.6°. The plane of the aromatic group approximately bisects the B(2)–B(3) vector in **1a** and the B(3)–C(8) vector in **1b**. There appear to be no other rotamer minima, in particular there is no apparent minimum for the plane of the aromatic group intersecting the B(2)–B(11) vector (Fig. 3).

Although the previously reported structure **1a** (Figs. 1 and 2, upper diagrams) is at an energetic minimum as confirmed by frequency analysis, we now report a second, lower, minimum **1b** (Figs. 1 and 2, lower diagrams). The two minima differ by about 48° in the rotational orientation of the phenyl group with respect to the heteroborane cluster, as measured by the cluster–P(7)C(8)–aromatic–C(*ipso*)C(*ortho*) dihedral angle. After these two minima were located, a calculational scan was performed about the dihedral angle in a hunt for any additional minima. A set of 36 optimizations was performed, each optimization having

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[1] Computational method: The two minima **1a** and **1b** were initially located and optimized with the STO-3G and 6-31G* basis sets, without symmetry constraints, using standard ab initio methods. The final optimization, frequency analysis (to confirm a true minimum in each case) and GIAO NMR nuclear shielding prediction were performed using B3LYP methodology as incorporated in the GAUSSIAN 98 package [3], and using the 6-31G* basis set. The other rotamer geometries were obtained using the optimized geometry for the previous rotamer as starting point, but with an additional 5° rotational twist; they were also optimized at B3LYP/6-31G*, with the dihedral angle fixed; frequency analyses were not performed, as these are not minima, but points on an intrinsic reaction coordinate. All final calculations carried out in this study were performed using the GAUSSIAN 98 package [3] on a home-assembled PC-Linux cluster-farm.

Table 1
Observed and calculated ^{11}B chemical shift values $\delta(^{11}B)$ (ppm) for [7-Ph-7,8,10-*nido*-$PC_2B_8H_{10}$] [a]

	Observed	Calculated rotamer **1a**	$\Delta\delta$	Calculated rotamer **1b**	$\Delta\delta$	Calculated 20:80 **1a**:**1b**	$\Delta\delta$
1	−39.7	−37.6	−2.1	−38.3	−1.4	−38.2	−1.5
2	−25.3	−25.6	+0.3	−23.4	−1.9	−23.8	−1.5
3	−8.0	−7.4	−0.6	−8.4	+0.4	−0.2	+0.2
4	−16.2	−15.6	−0.8	−17.7	+1.5	−17.2	+1.0
5	−16.8	−14.9	−1.9	−15.8	−1.0	−15.6	−1.2
6	−8.7	−8.8	+0.1	−9.2	+0.5	−9.2	+0.5
9	−7.6	−7.4	−0.2	−7.2	−0.4	−7.2	−0.4
11	−13.7	−8.4	−4.3	−14.1	+0.4	−13.2	−0.5

[a] Calculated ^{31}P shieldings for the two rotamers differ by 12.7 ppm, and the calculated ^{13}C shieldings of C(8) and C(10) differ by 10.4 and 4.9 ppm, respectively.

a fixed dihedral angle at 5° intervals in the range 0–175°; no other minima were found (Fig. 3).

The configuration of the second minimum **1b** is at first sight somewhat surprising, as the *ortho* aromatic hydrogen atoms are in quasi-eclipsing positions with respect to the β cluster hydrogen atoms on B(3) and B(11). This is one reason why we did not initially examine for an energetic minimum in this area. There is an obvious general caveat here. A second caveat is that, if lower-level initial calculations are used to find an approximate minimum, which is thence further refined at the higher calculational level, as was the case in work in Ref. [9], other important minima may be missed. In this regard, in terms of iterative energetic minimizations, it can be seen from Fig. 3 that there is an approximately 110° catchment area for rotamer **1b** and a 70° catchment area for rotamer **1a**.

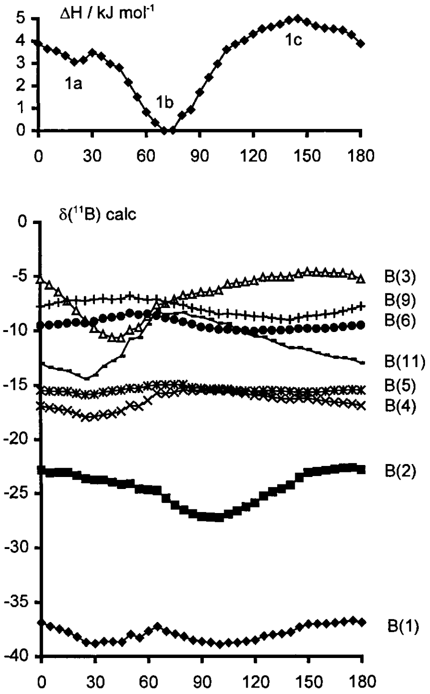

Fig. 3. Calculated (DFT B3LYP/6-31G*) enthalpy variation ΔH (uppermost trace) and GIAO chemical-shift profiles (lower traces) for the contrarotational fluxionality about the P(7)–C(aryl) bond in [7-Ph-7,8,10-*nido*-$PC_2B_8H_{10}$] (**1**). The horizontal axis has an arbritrary rotational zero origin. The apparent non-isotonic variation of $\delta(^{11}B)$ with angle arises because of the extreme sensitivity of the GIAO shielding calculations to geometry allied with the slightly inexact positions of the calculated structures with respect to the exact true minima, which were often somewhat 'loose'. There is no minimum **1c** that would otherwise correspond to configuration **1a** (i.e. with the aromatic plane approximately eclipsing the CH(8) unit and approximately bisecting the B(2)–B(11) vector), expected at an angle of ca. 140° on this scale; on the contrary, this is near the calculated energetic maximum.

The quasi-eclipsed configuration **1b** merits some comment. The distances between the aromatic *ortho* hydrogen atoms and the cluster β hydrogen atoms on B(3) and B(11) at 2.287 and 3.070 Å are not particularly short, suggesting only a small 'non-bonded' interaction, which would normally be regarded as repulsive, although the possibility of attractive C–H–H–B dihydrogen bonding cannot be excluded. However, such interactions would be comparable to those in conformer **1a** in which the comparable distances to B(2) and B(3) are 2.481 and 2.528 Å, respectively. Some electronic control of configuration is therefore implied, particularly so because there is no minimum associated with a corresponding opposing rotamer **1c** that would approximately eclipse the cluster β hydrogen atom on C(8) with the aromatic ring hydrogen atom (Fig. 3). On the contrary, this last configuration is in fact very close to an energetic maximum.

The electronic change between **1a** and **1b** is reflected in a geometrical flexing, manifested most obviously in a decrease in the P(7)–C(8) and P(7)–B(11) distances of 0.016 and 0.015 Å, respectively, from **1a** to **1b**. The electronic change is also manifested in significant nuclear shielding changes. The calculated ^{11}B shieldings for this second rotamer **1b** now much more closely match the observed values. In particular the −4.3 ppm anomaly for $^{11}B(11)$ is reduced to an acceptable magnitude of +0.4 ppm. This close matching implies that the rotamer **1b** dominates the rotamer population and thence is energetically the more stable. This greater stability may be reflected in the shorter P(7)–C(8) and

P(7)–B(11) distances for **1b** just mentioned. Although relative energies among structures calculated at the B3LYP/6-31G* level are recognized as not being absolutely reliable for small differences like these, particularly as they refer to the gas-phase, and the experimental results for compound **1** are obtained in a condensed phase, the implied dominance by rotamer **1b** is nevertheless reflected in the calculated difference in energy between **1a** and **1b**, a difference δH of ca. 3.5 kJ mol^{-1}. A reasonable assumption of minimal entropy differences among rotamers would thence suggest an approximately 20:80 population ratio for **1a**:**1b** in the rotamer mixture at room temperature. In this context, it is noted that a 20:80 **1a**:**1b** weighted average of the calculated chemical shifts gives a slightly better overall agreement with experiment (Table 1, final columns), although it may be inappropriate to read too much into this degree of refinement of the approach, given the experimental and calculational uncertainties involved. The energy profile for the entire rotation, calculated at the B3LYP/6-31G* level, is given in Fig. 3, from which it can be seen that **1a** and **1b** are the only minima, as mentioned above. The energetic maximum for the whole cycle gives a computed activation enthalpy $\Delta H^{\ddagger}$ of ca. 5.0 kJ mol^{-1}, consistent with the relatively free rotation as it would imply a rotational frequency of $> 10^{10}$ Hz at room temperature. Fig. 3 also shows that the extremes of chemical shift variation for the various sites do not coincide with each other, or with the energetic maxima or minima of the rotation. This is particularly apparent for the three sites that show the maximum variation, viz. B(2), B(3) and B(11) conjoined to the phenyl-substituted P(7) vertex, which show variations of ca. 4.8, 6.0 and 6.1 ppm, respectively, the other variations having smaller ranges of 1.0–2.5 ppm. Of these, however, the extremes for the B(11) nuclear shielding do happen to approximate reasonably closely to the two minima, resulting in the large calculated difference $\Delta\delta$ of 4.7 ppm (Table 1) and in the anomalous discrepancy between experimental and calculated shieldings that was noted in Ref. [9].

There are two related conclusions to this work. Firstly, although the boron-containing clusters in this type of compound are ostensibly rigid, the results demonstrate a significant differential effect on the cluster geometry and cluster nuclear shielding arising from different *exo*-bond rotamers. This is likely to be a general phenomenon, and likely to be most marked for π-interactive substituents, for example unsaturated groups or groups with lone pairs α to the cluster. It is obviously important to consider contributions from all bond rotamers in predictions of nuclear shielding, particularly when the rotamers are of similar energy. In this regard, our results suggest that lower-level calculations may not reveal all rotamer minima, and so, if used to pinpoint approximate minima, which are then subsequently refined at a higher calculational level, other important minima may be overlooked. Secondly, and implicit in the nuclear shielding and geometrical changes within the cluster, is that the differences between rotamers in their bonding *exo* to the cluster are manifested in changes in the cluster molecular orbitals. In this present example, the bonding involving the cluster atoms adjacent to a phenyl-substituted site is most affected. In the general case, however, there is the possibility that more extended cluster molecular orbitals may be involved, so that effects distal from the substituent, e.g. in antipodal positions, might be observable, and that, in extreme cases, much more significant distortions of the cluster geometry may occur. Again, these effects are likely to be most marked for π-interactive substituents [10,11]. Related effects will obtain in transition-element/borane systems that exhibit rotational fluxionality [12].

1. Supplementary material

Coordinates for the DFT B3LYP/6-31G* calculated structures of the two energy-minimum rotamers **1a** and **1b** of [7-Ph-7,8,10-*nido*-$PC_2B_8H_{10}$] are available from the relevant authors (e-mail: johnk@chem.leeds.ac.uk and danielo@chem.leeds.ac.uk). They, together with an animation of the rotational process, are also to be found at http://www.chem.leeds.ac.uk/boronweb/ormsby/animations/

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