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Is diphenylboronium perchlorate in nitromethane ionic?

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Abstract—The ^{11}B NMR chemical shift for diphenylboronium perchlorate was determined to be 46.02 ppm in CD_3NO_2. An ab initio calculation of the chemical shift (GIAO-HF/6-311+G(2d,p)//B3LYP/6-31+G(d)) indicated a value of 47.02 ppm. The agreement between the calculated and found values strongly suggests that the character of the B–O bond is covalent with an ionic character. © 2001 Elsevier Science Ltd. All rights reserved.

Davidson and French[1] observed that the addition of silver perchlorate to a solution of chlorodiphenylborane in nitrobenzene resulted in the immediate precipitation of silver chloride. They noted that the foregoing metathesis reaction occurred only in polar solvents and that the cationic boron species could be isolated only as the 2,2′-bipyridyl complex $[(C_6H_5)_2B(bpy)]^+ClO_4^-$, mp 320°C (Scheme 1). Earlier reports,[2] however, on the structure of the historical boronium cation have been questioned; several structures were postulated, based on the studies on its conductance, UV spectra and ^{1}H NMR spectra with MO calculation at a lower level, as shown in Fig. 1. Up-to-date investigations are awaited and are necessary for a comprehensive understanding of the unambiguous structure of the cation. The expected Lewis acidity of the boronium ion, available for organic reactions,[3] is of interest in connection with the long-standing question of the nature of the ionic species. We disclose herein the same evidence on the nature of diphenylboronium perchlorate, which is derived from a quantum chemical ab initio calculation of molecular structures related to Fig. 1 and a correlation between the calculated ^{11}B NMR chemical shifts and the experimental data.

^{11}B NMR spectra (concentration: 0.5 M solution in CD_3NO_2) were measured at 128 MHz with a JEOL JNM-LA 400 spectrometer (at 21.6°C, number of accumulations: 400). Chemical shifts are expressed in ppm downfield from $BF_3{\cdot}OEt_2$. When a solution of $AgClO_4$ in CD_3NO_2 was added to a solution of chlorodiphenylborane at rt under an argon atmosphere, AgCl precipitated from the pale yellow solution, after which it became colorless. After filtration of the precipitate, NMR spectra of the solution were measured. At this point, 2,2′-bipyridyl was added to the solution of diphenylboronium perchlorate, followed by continuous NMR measurements. Surprisingly, the observed ^{11}B chemical shift of diphenylboronium perchlorate was found to be 46.02 ppm, which is considerably higher than that (61.87 ppm) of the starting chloride: the

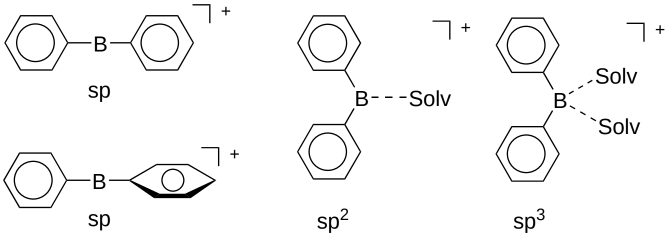
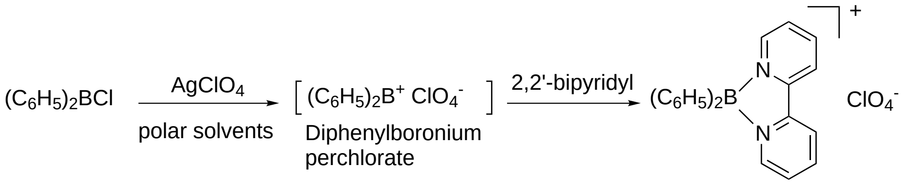


Figure 1.



Scheme 1.

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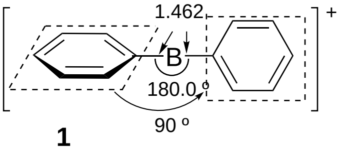
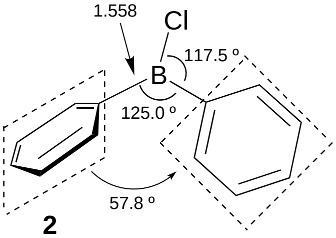
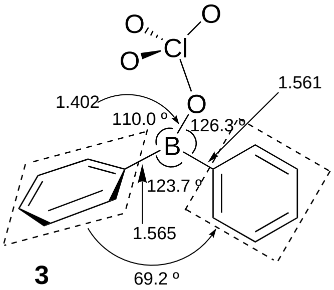
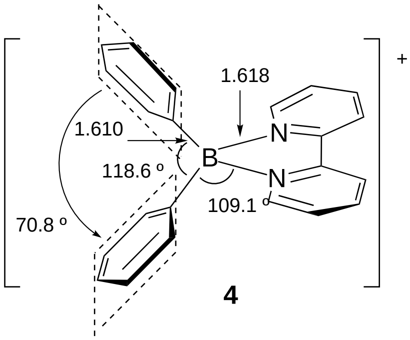
higher field shift is inconsistent with the expected cationic character, which would be accompanied by a decrease in electron density.[4] The ^{11}B chemical shift of the 2,2′-bipyridyl complex was observed at 6.37 ppm which is typical for four-coordinate boron.

The structures were optimized at the B3LYP/6-31+G(d) level. ^{11}B chemical shift calculations were done using the GIAO approach[5] with the HF method B3LYP and the 6-311+G(2d,p) basis set. All quantum chemical calculations were carried out with the GAUSSIAN 98 program suite.[6] The results are summarized in Table 1. The optimized structure of the free diphenylboronium ion was found to be a linear structure, **1**, where two phenyl rings are perpendicular and the *ipso*-C–B bonds have been shortened, compared with that of **2**. The ^{11}B chemical shift of **1** was calculated to be 85.49 ppm (from the standard of $BF_3·OEt_2$),[7] at considerably downfield, as expected for its free cation. The calculation starting with boron cation **1** and perchlorate ion resulted in the optimized structure, depicted as **3** and, using this structure, the ^{11}B NMR shift of **3** was then calculated. Surprisingly the calculated shift, 47.02 ppm, is very similar to the observed value, 46.02 ppm.[8] The agreement between the calculated and found values suggests that the actual structure of diphenylboronium

Table 1. Optimized structures and the correlation of experimental and calculated ^{11}B NMR shifts

structure[a]	experimental[b] in CD_3NO_2 (ppm)	calcd[c] (ppm)
 **1**	—	85.49
 **2**	61.87	59.63
 **3**	46.02	47.02
 **4**	6.37	8.06

[a] Optimized structures using B3LYP/6-31+G(d). [b] ^{11}BNMR spectra were measured in CD_3NO_2 at rt. The chemical shifts are expressed in ppm downfield from $BF_3·OEt_2$. [c] Calculated using GIAO-HF/6-311+G(2d,p) for B3LYP/6-31+G(d) optimized structures.

perchlorate may not be far from the optimized structure **3**. From this structure, the B–O bond, 1.402 Å, is covalent having ionic character at a lower level, compared with the standard value, 1.363 Å, for a single B–O bond.[9] The cation moiety of the 2,2′-bipyridyl complex was also calculated using the same procedures and a good correlation between the experimental and calculated ^{11}B NMR shifts were obtained. The result indicates that the 2,2′-bipyridyl complex is almost surely derived by addition of 2,2′-bipyridyl to the chemical species, depicted by structure **3**.

In conclusion, some evidence is provided relative to the long-standing problem of the structure of the historical boron cation, diphenylboronium perchlorate. The reported evidence was obtained from a correlation of experimental and calculated ^{11}B NMR shifts and suggest that the diphenylboronium ion is bonded to perchlorate ion via a covalent bond with an ionic character.[9]

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7. The absolute shielding value was obtained for $BF_3{\cdot}OEt_2$, which was optimized according to the same procedures (GIAO-HF/6-311+G(2d,p)//B3LYP/6-31+G(d).
8. The calculated ^{11}B chemical shift of the solvent-coordinated species, starting from the free diphenylboronium ion and one nitromethane, found to be 54.50 ppm (with a B–O bond length of 1.545 Å), which is far from the observed value while the calculation on the species involving two solvent molecules could not be converged.
9. *Tables of Interatomic Distance and Configuration in Molecules and Ions*; Sutton, L. E., Ed.; Chemical Society: London, 1958. The level of the ionic character on the B–O bond of diphenylboronium perchlorate was evaluated, compared with that of Ph_2BOH (the former: B–O bond length 1.402 Å; Mulliken charge B 0.680, O −0.541, the latter: B–O bond length 1.375 Å; Mulliken charge B 0.553, O −0.240).