Conformation of the Tetraphenylborate Ion

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Sir:

A conformational study on an idealized model of the tetraphenylborate ion, based on consideration of atom pair interactions, has been reported.[1] It has shown that rotations of the phenyl groups about their axis in the anion are hindered to a larger extent than in similar ions (e.g., $AsPh_4^+$ or PPh_4^+). Recent structural investigations[2-4] have essentially confirmed the results of calculations, as the scatter of values of the inter-phenyl angles has never been found to be high. By purely qualitative reasoning, the limited flexibility of the bulky BPh_4^- anion could contribute to stabilize particular conformations of complex cations in the solid phase; e.g., this could be the case with the $[Co(np_3)I]^+$ cation [np_3 = tris(2-diphenylphosphinoethyl)amine], which attains the high-spin state and related geometry[5,6] in the solid state only when the BPh_4^- counterion is used.

Recently, the conformational study on BPh_4^- has been extended[4] to consider the effects of deviations from regular tetrahedral geometry about the boron atom. Stabilization by ca. 2 kcal mol^{-1} has been found in a particular case, with respect to the regular model.[1] This has been attributed[4] to the inclusion of terms due to the tertiary carbon atoms into the energy expression. I wish to point out that all contributions to the conformational energy by the tertiary carbon atoms, likely to affect the shape of the energy surface, were already included in the previous[1] calculation. Only interactions *within* the set of four tertiary carbon atoms were neglected, as these contribute a constant (and large, repulsive: ca. 8.5 kcal mol^{-1}) term to the energy, in the regular conformation. Inclusion of this term, which is sensitive to distortions from the regular geometry (even to small distortions, in the limit of experimental error) may prevent significant comparisons between the regular and nonregular geometries. Comparisons, in order to be significant, should account in addition for the contribution to the energy by the large number of terms due to bending, stretching, etc., deformations. These were neglected before,[1] as considerations were restricted to the case of idealized geometry.

The conformational energy of the anion in the two complexes (a) $[Co(np_3)I]BPh_4$ and (b) $[Ni(nas)NCS]BPh_4$ {nas = *N,N*-bis[2-(diethylaminoethyl)]-2-(diphenylarsinoethyl)amine}, which had been considered before,[1] has been calculated following the procedure previously described.[1] In the present calculation the experimental atomic positions have been used, rather than those calculated for the regular anion[1] in the conformation having inter-phenyl angles equal to those found experimentally. The energy differences [E(real) − E(idealized model)] are (a) 0.1 and (b) −5.3 kcal mol^{-1}. The "stabilization" in case b is larger than that calculated in ref 4, even though no changes have been imposed now on the form of the energy expression. This result warns against attempting to make quantitative estimates of the stabilization of the complex in the solid phase, based on consideration of the deformations undergone by the anion. Reliable estimates would require improved models for calculations both in the regular and in the nonregular geometries.

Registry No. BPh_4^-, 4358-26-3.

References and Notes

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