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Intramolecular proton transfer in $[Ph_2B–OH_2]^+$. Participation of a phenyl group

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***Ab initio* calculations at the HF/6-31+G* level on $[Ph_2B–OH_2]^+$ show that in the gas phase the structure with the proton attached to an ipso C is lower in energy than the one with the proton on the oxygen atom by 8.40 kcal mol^{-1}. The transition states and reaction paths for intramolecular proton transfer in $[Ph_2B–OH_2]^+$ have also been studied.**

Intramolecular proton transfer (in the ground state) generally involves electronegative atoms like O or N. In many cases, such as keto-enol tautomerism, an alkyl C atom is involved[1] and the hybridization of the C atom shuttles between sp^2 and sp^3. However, participation of a phenyl C in such phenomena is, to our knowledge, hitherto unknown. In the keto-enol tautomerism of phenol, involvement of a phenyl C atom can be postulated but thermodynamically the equilibrium lies well to the phenol side.[1] Herein, we report a case of intramolecular proton transfer (in the ground state) where thermodynamically the arenium side is favoured.

The species we have studied is $[Ph_2B–OH_2]^+$. Its existence is implicated in the electrochemical oxidation of the tetraphenylborate anion, $[BPh_4]^-$, in water.[2,3] It is generated in the following disproportionation reaction:

$$2\ Ph_3B–OH_2 = [Ph_2B-OH_2]^+ + [BPh_4]^- + H_2O$$

The structure of $[Ph_2B–OH_2]^+$ (I), was investigated using Gaussian98 at the HF/6-31+G* level.[4] First the two torsion angles around the B–C(Ph) bonds were varied in 30° intervals to find the lowest energy conformation of the cation. This proved to have C_2 symmetry with torsion angles (for C7–C2–B1–C8 and C2–B1–C8–13) of 149.3° as shown in Fig. 1.

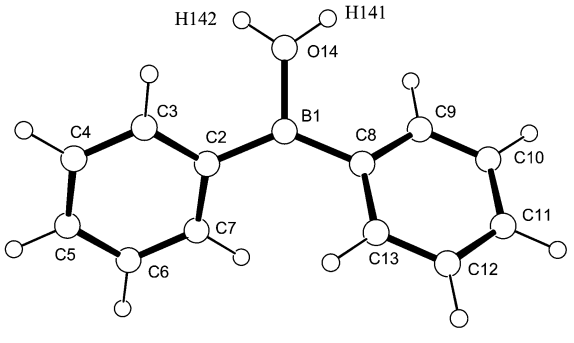

Fig. 1 The optimized structure of $[Ph_2B–OH_2]^+$ (I) at the HF/6-31+G* level showing the atomic numbering scheme. The structure has C_2 symmetry. Selected electrostatic potential charges: H141 0.488, O14 −0.616, B1 0.530, C2 −0.172, C3 −0.110, C7 0.002

The dimensions of this optimized structure are listed in Table 2. The boron atom has a trigonal environment.

Proton transfer can be envisaged to occur from the oxygen atom O14 to any of the carbon atoms in a phenyl ring, namely C8 to C13 inclusive. Transfer to the other phenyl ring is of course equivalent. Accordingly hydrogen atoms were positioned on each carbon atom in turn. This gave six possible structures, all of which were geometry optimized at the HF/6-31+G* level using the Gaussian98 program. The resulting energies are given in Table 1 and the lowest energy structure was found to be structure II, shown in Fig. 2, in which the hydrogen atom is located on C8. Structure III in which the hydrogen atom migrates to C9 is higher than II in energy by 2.87 kcal mol^{-1}.

These calculations show that for $[Ph_2B–OH_2]^+$ in the gas phase, structure II where the proton is located on the ipso carbon C8 (Fig. 2) is energetically lower than when the hydrogen atom is located on the oxygen atom, structure I (Fig. 1) by 8.40 kcal mol^{-1}.[5–7] Indeed, it is interesting to note that lower energies are obtained when the hydrogen is positioned on any of the carbon atoms of the phenyl ring. The three structures I, II and III were then geometry optimized using density functional theory at the B3LYP/6-311+G* level and energies of −564.48 723, −564.49 676, −564.49 036 a.u. were obtained (relative energies 5.84, 0.00, 3.87 kcal mol^{-1}); these results are similar to those obtained with the HF/6-31+G* basis set.

The theoretically determined bond parameters for the two structures I and II are compared in Table 2. In both structures, the boron atom is trigonal planar. In structure II, the ipso C bearing the proton is distorted tetrahedral and the two C–C bonds, C8–C9 and C8–C13, both increase from their mean aromatic value of 1.404 Å in I to 1.453 and 1.457 Å, a distance that is indicative of some residual double bond character. Conversely, the adjacent carbon bonds C9–C10 and C12–C13 increase their double bond character with distances decreasing to 1.363 and 1.362 Å, respectively. Obviously, in structure II,

Table 1 The energies obtained at the HF/6-31+G* level after convergence of the structures with different positions of the proton in $[Ph_2B–OH_2]^+$

Proton Position	Energy/a.u.	Relative energy/kcal mol^{-1}
C8	−560.79145	0.00
C9	−560.78688	2.87
C10	−560.78746	2.50
C11	−560.78593	3.46
C12	−560.78826	2.00
C13	−560.78387	4.76
O14	−560.77806	8.40

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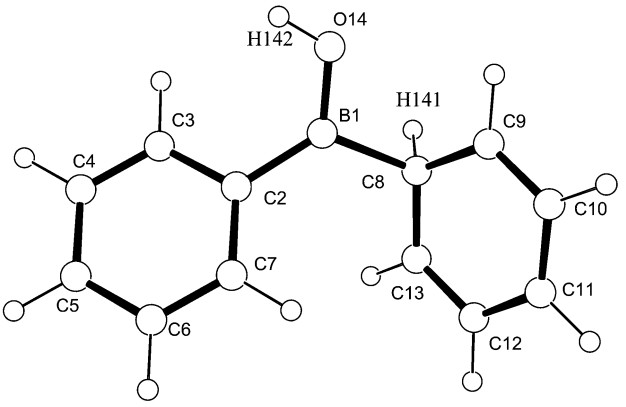

Fig. 2 The lowest energy structure obtained (II) at the HF/6-31+G* level after proton transfer from O14 to C8. Selected electrostatic potential charges: H141 0.071, H142 0.453, O14 −0.709, B1 0.619, C2 −0.328, C3 −0.030, C7 0.052, C8 0.090, C9 0.097, C13 0.108.

we have an arenium ion in which the proton is σ-bonded to a C atom.

Very recently, from IR spectroscopy Solca and Dopfer have concluded[8] that for the benzenium ion, $C_6H_7^+$, the σ-bonded species is more stable than the π-bonded one (having proton-π interactions) in the gas phase. Still, in our case, we examined the possibility of a π interaction by considering starting models in which the proton interacted with a combination of carbon atoms. The proton was included at various positions above the phenyl ring. It was placed equidistant from all six carbon atoms and at various distances above the plane of the ring, but in all cases, the starting position proved unstable and the hydrogen moved so that its final position after geometry convergence was bonded to one carbon atom only. It therefore seems unlikely that some kind of proton-π interactions occur after proton transfer.

The mechanism for proton transfer from structure I to structure II was then considered. The transition state TS1 was obtained at the HF/6-31G//6-31+G* level by using the QST3 procedure in Gaussian98 and confirmed as such by having one negative frequency at −2022.6 cm^{-1}. The structure of the transition state is shown in Fig. 3.

Table 2 Selected bond distances (in Å) and angles (in degree) in the theoretically determined structures I, TS1 and II

	I	TS1	II
O14–141	0.950	1.304	2.514
C8–H141	2.709	1.415	1.095
O14–H142	0.950	0.969	0.950
B1–O14	1.513	1.443	1.335
B1–C8	1.532	1.612	1.706
B1–C2	1.532	1.511	1.555
C8–C9	1.406	1.421	1.453
C9–C10	1.381	1.373	1.363
C10–C11	1.391	1.390	1.401
C11–C12	1.387	1.390	1.405
C12–C13	1.385	1.373	1.362
C13–C8	1.402	1.421	1.457
H141–O14–H142	114.2	133.4	116.9
H141–O14–B1	122.9	79.2	–
H142–O14–B1	122.9	147.4	–
O14–B1–C8	112.8	96.4	113.2
O14–B1–C2	112.8	128.3	126.4
C8–B1–C2	134.4	135.3	120.3
B1–C8–C9	122.6	120.6	108.9
B1–C8–C13	119.2	120.6	103.9
C9–C8–C13	118.2	117.8	116.0
B1–C2–C3	122.6	120.1	123.4
B1–C2–C7	119.2	121.3	118.6
C3–C2–C7	118.2	118.6	118.0

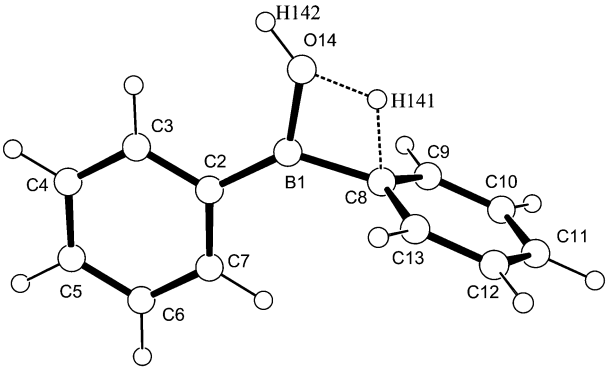

Fig. 3 The structure of the transition state TS1 between structures I and II showing proton transfer from O14 to C8.

The geometry of this transition state TS1 is compared to those of I and II in Table 2. The geometry is for the most part intermediate between I and II, but it is noteworthy that the boron maintains its trigonal environment and that the O14–H141 and C8–H141 distances for the migrating proton are not too dissimilar at 1.304 and 1.415 Å, respectively. However, the most interesting feature of the transition state is that the C7–C2–B1–C8 and C2–B1–C8–C9 torsion angles are 180.0° and 84.3°, respectively, and as in addition the H141–O14–B1–C8 torsion angle is 0.0° it is apparent that the structure possesses approximate C_s symmetry.

We also investigated the transition state for structure III with the hydrogen atom located on C9 and obtained an optimized transition state, using the QST3 method at the HF/6-31G//6-31+G* level, called TS2 and shown in Fig. 4. This structure contains one negative frequency at −2075.8 cm^{-1}.

We then used the IRC method available in Gaussian98 to obtain the reaction coordinate energy profiles for TS1 and TS2. The results of these calculations confirm that these transition states TS1 and TS2 do indeed connect I and II, and I and III, respectively, with the proton being transferred from O14 to C8 or C9. It is interesting to note that the energy of this transition state TS2 at the HF/6-31G//6-31+G* level is −560.72 620 a.u., significantly less than that observed for TS1, which is −560.71 580 a.u. although the energies of the final structures show that II lies below III by 2.9 kcal mol^{-1} at the HF/6-31+G* level. This result is consistent with the observation, apparent from Fig. 3 and 4, and the parameters in Table 2 that TS1 is more strained than TS2, in that the structure involves a strained four-membered ring (comprising B1, O14, H141 and C8) while TS2 contains a relatively unstrained five-membered ring.

Release of a proton from the cationic species $[Ph_2B–OH_2]^+$ yields diphenylboronic acid $Ph_2B–OH$. Thus, $[Ph_2B–OH_2]^+$

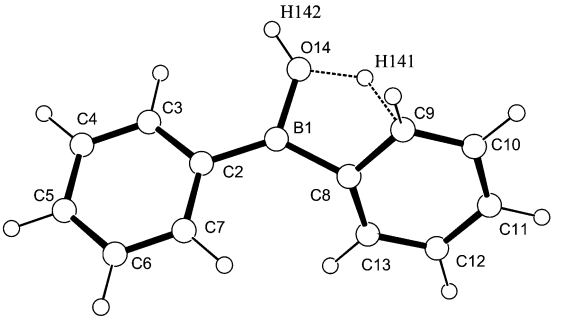

Fig. 4 The structure of the transition state TS2 between structures I and III showing proton transfer from O14 to C9 .

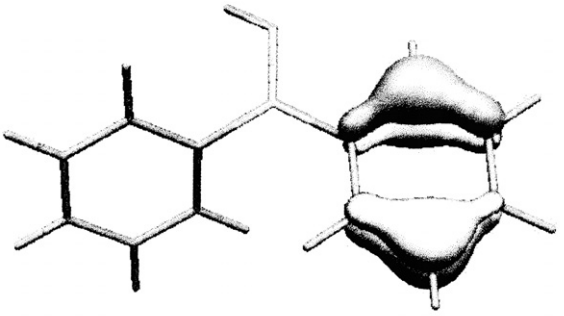

Fig. 5 The HOMO in Ph_2BOH.

can be regarded as a protonated form of Ph_2B–OH. An interesting consequence of our present work is that if one tries to protonate Ph_2B–OH, the added proton is likely to prefer one of the ipso carbons rather than the oxygen atom for attachment although the oxygen atom in Ph_2B-OH is found to bear a more negative charge (−0.707) than the two ipso C atoms (−0.110, −0.059). However, as shown in the HOMO of Ph_2B–OH is located on the phenyl ring though with a higher contribution from C9 than from C8 or C10.

Our work is consistent with other studies on the preferred site of protonation of substituted aromatic in the gas phase.[7,9,10] Of particular relevance to this work is the study of substituted anilines[7] in which calculations at the B3LYP/6-311G**++//B3LYP/6-31G**+ZPE(B3LYP/6-311G**) level showed that for para-substituted anilines amine protonation is favoured over ring protonation while for meta-substituted anilines, ring protonation is favoured. However, the difference in proton affinity for both meta and para substituents is very dependent upon the electron-donating ability of the substituent. Indeed, experimental results for *m*-anisidine, *m*-thiomethylaniline and *m*-ethylaniline have shown protonation on the benzene ring in the gas phase and this has been ascribed to the increased electron density (relative to aniline) on the benzene ring.[11]

Arylboronic acids are chemically very important compounds.[12,13] Very recently Mori *et al*[14] have used Ph_2B–OH as a catalyst for stereoselective aldol reactions in water. Diphenylboronic acid also has the potential for sensing saccharides.[15] Our present studies add a new dimension to the chemistry of diphenylboronic acid.

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