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The intrinsic (gas-phase) acidities of bridgehead alcohols
An experimental (FT-ICR) and computational study

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Abstract

The gas-phase acidities of 1-adamantanol and perfluoro1-adamantanol were determined by means of Fourier transform ion cyclotron resonance spectrometry (FT-ICR). The acidity of perfluoro1-adamantanol seems to be the highest ever reported for an alcohol. A computational study of these species and their anions at both the MP2/6-311 + G(d,p) and B3LYP/6-311 + G(d,p) levels was performed. Also studied were the tertiary alcohols (including their perfluorinated forms) derived from norbornane, bicyclo[2.2.2]octane and cubane. It was found that: (i) the intrinsic acidity of non-fluorinated bridgehead alcohols increases with the strain of the hydrocarbon framework and, (ii) perfluorination of these compounds strongly increases their acidity and, likely, significantly modifies their internal strain.

Keywords: Ab initio; 1-Adamantanol; Bridgehead alcohol; FT-ICR; Perfluoro1-adamantanol

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1. Introduction

We have long been interested in the relationship between structure, thermodynamics and reactivity of neutral and ionic species in the gas phase. Of particular importance are the acidity and basicity of species A–H(g), and the basicity of species B(g), respectively measured by $\Delta_r G^\circ_m$(AH) and $\Delta_r G^\circ_m$(B), the standard Gibbs energy changes for reactions (1) and (2):

$$\text{A–H(g)} \rightarrow \text{A}^-\text{(g)} + \text{H}^+\text{(g)} \quad (1)$$

$$\text{B(g)} + \text{H}^+\text{(g)} \rightarrow \text{(BH)}^+\text{(g)} \quad (2)$$

Here, and for the sake of simplicity, we shall replace $\Delta_r G^\circ_m$(AH) by *GA*(AH), a simplification of the symbol $\Delta_{acid}G$(AH) used in the NIST Chemistry WebBook [1].

Gas-phase acidities and basicities are valuable for the unraveling of reaction mechanisms [2,3], the development of new, super-strong acids and bases [4,5], and the design of stable anions of very low nucleophilicity and high industrial relevance [6,7].

The reactivity of adamantane, a highly symmetrical molecule (T_d) [2] (Fig. 1) and the thermodynamic stability of its derivatives [8], including the carbenium ions and radicals derived therefrom [8,9] have been one of our subjects of interest. 1-Adamantyl cation is "protected" by Bredt's effect [10].

According to the Taft-Topsom model of substituent effects on gas-phase reactivity [11,12], the 1-adamantyl group is endowed with a large polarizability, as defined by the parameter σ_α. This property is an important factor in determining the gas-phase acidity and basicity of a variety of organic compounds. Even in solution, the basicity of simple monomeric aliphatic primary, secondary and tertiary alcohols (ROH) including 1-adamantanol, significantly increases with the polarizability of the substituent R [13].

It was shown in 1979 that, in the gas phase, 2,2,2-trifluoroethanol is ca. 70 kJ mol^{-1} more acidic than ethanol

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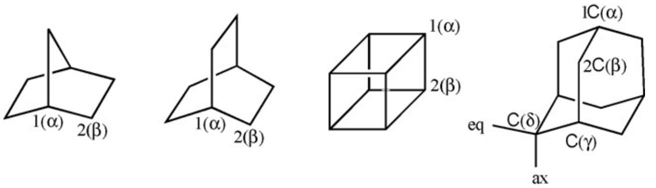

Fig. 1. From left to right, structures of norbornane, bicyclo[2.2.2]octane, cubane and adamantane.

[14]. Later work on fluorinated alcohols such as 1,1,1,3,3,3-hexafluoro-2-propanol and perfluoro-*tert*-butyl alcohol [15] showed the important acidity-enhancing effect of further fluorination.

All these reasons have prompted us to use Fourier transform ion cyclotron resonance spectrometry (FT-ICR) [16] to determine the gas-phase acidity of 1-adamantanol and perfluoro1-adamantanol as well as to carry out a computational study of these species and their anions. Because internal strain and hyperconjugative effects are relevant factors to be taken into consideration [17,18], the study was extended to 1-norbornanol,1-bicyclo[2.2.2]octanol, cubanol, and their perfluorinated derivatives. Their corresponding hydrocarbon frameworks are also shown in Fig. 1.

2. Experimental

2.1. Materials

Perfluoro1-adamantanol, a gift from Idemitsu Kosan Co. Ltd., was carefully dehydrated by three successive sublimations.

1-Adamantanol (Merck, 99%) was crystallized in hexane and twice sublimed.

2.2. Gas phase studies

2.2.1. The FT-ICR spectrometer

In this work, use was made of a modified Bruker CMS 47 FT-ICR mass spectrometer. A detailed description of the original instrument is given in Ref. [19]. It has already been used in a number of recent studies [3,20]. Some salient features are as follows: The spectrometer is linked to an Omega Data Station (IonSpec, CA). The high-vacuum is provided by a Varian TURBO V550 turbomolecular pump ($550\,\mathrm{l\,s^{-1}}$). The magnetic field strength of the superconducting magnet is 4.7 T.

2.2.2. Determination of gas-phase acidities [1]

Mixtures of perfluoro1-adamantanol, or 1-adamantanol, ROH, and a reference acid $A_{ref}H$ of known gas-phase acidity were introduced into the high vacuum section of the instrument. Typical partial pressures were in the range 2×10^{-8} to 1×10^{-7} mbar. The average temperature of the cell was ca. 331 K. *iso*-Amyl nitrite, *iso*-$C_5H_{11}NO_2$, containing ca. 20% of methanol, was added (nominal pressures of ca. $2–3\times10^{-8}$ mbar). Resonant capture of electrons provided a mixture of *iso*-amyl alkoxide and methoxide anions. In cases wherein the total pressures were below 2×10^{-7} mbar, argon was added up to a total pressure of this order. After reaction times of 8–12 s, all *iso*-$C_5H_{11}O^-$ and CH_3O^- were protonated by ROH and $A_{ref}H$, this leading to a mixture of RO^- and $A_{ref}{}^-$. Systematically, one of these ions was isolated by means of ion-selection techniques and allowed to react with the neutral species, the system being monitored during 10–25 s.

In all cases, it was established that reaction (3) had reached a state of equilibrium during this time:

$$\mathrm{ROH(g)} + \mathrm{A_{ref}{}^-(g)} \rightleftarrows \mathrm{RO^-(g)} + \mathrm{A_{ref}H} \quad K_\mathrm{p} \quad \Delta_\mathrm{r}G^\circ_\mathrm{m} \tag{3}$$

Thus, from experiment to experiment, the limiting ratio of abundances of the two ions remained constant within 5%, irrespective of whether ions $A_{ref}{}^-$ or ions RO^- were selected. In other experiments, no selection was carried out, but the ratio was the same, within these limits. In each case, the K_p values are the average of six different experiments involving different ratios of the pressures of the neutral bases. The results are seen to be nicely consistent. The experimental results are summarized in the following section.

The pressures of the neutral species were measured with a Bayard-Alpert ion gauge. Its readings were corrected according to the method by Bartmess and Giorgiadis [21], using for each compound, the polarizabilities α(ahc) calculated following Miller's method [22].

By definition, the gas-phase acidity of ROH, *GA*(ROH) is the standard Gibbs energy change for reaction (4), $\Delta_\mathrm{r}G^\circ_\mathrm{m}$ (4).

$$\mathrm{ROH(g)} \rightarrow \mathrm{RO^-(g)} + \mathrm{H^+(g)} \quad \Delta_\mathrm{r}G^\circ_\mathrm{m} \tag{4}$$

Its value can be determined from $GA(A_{ref}H)$ and K_p through Eq. (5):

$$GA(\mathrm{ROH}) = GA(\mathrm{A_{ref}H}) - RT\ln K_\mathrm{p} \tag{5}$$

2.2.3. Experimental results

The experimental results obtained as indicated above are summarized in Tables 1 and 2.

The estimated uncertainties, 0.9 and $1.4\,\mathrm{kJ\,mol^{-1}}$ are twice the standard deviation of the average. Notice however that, although the precision is satisfactory, the accuracy of the various $GA(A_{ref}H)$ values is given as $8.4\,\mathrm{kJ\,mol^{-1}}$ [23] and we estimate the same uncertainty for our data.

It is important to notice that the anions 1-$C_{10}H_{15}O^-$ and 1-$C_{10}F_{15}O^-$ do not show any sign of decomposition (as this would lead to the appearance of fragment ions) during reaction times

Table 1
Experimental results (in $\mathrm{kJ\,mol^{-1}}$) pertaining to the determination of the gas-phase acidity of perfluoro1-adamantanol, *GA*(ROH)

$A_{ref}H$[a]	$GA(A_{ref}H)$[a,b]	$RT\ln K_p$[a]	*GA*(ROH)[a]
$CF_3(CF_2)_2CO_2H$	1318.0	−2.46 ± 0.35	1320.46
CF_3CO_2H	1323.0	2.20 ± 0.69	1320.80
$C_6F_5CO_2H$	1325.0	3.65 ± 1.14	1321.35
o-$C_6H_4(OH)CO_2H$	1330.0	9.70 ± 1.06	1320.30
Average			1320.7 ± 0.9

[a] Defined in the text.
[b] Taken from Ref. [1].

Table 2
Experimental results (in kJ mol^{-1}) pertaining to the determination of the gas-phase acidity of 1-adamantanol, *GA*(ROH)

$A_{ref}H$[a]	*GA*($A_{ref}H$)[a,b]	$RT \ln K_p$[a]	*GA*(ROH)[a]
CH_3CN	1528.8	−1.92 ± 0.17	1530.72
C_2H_5CN	1537.2	6.02 ± 0.64	1531.20
c-C_3H_5CN	1538.9	8.92 ± 0.70	1530.00
i-C_4H_9OH	1539.7	10.03 ± 0.14	1529.67
Average			1530.4 ± 1.4

[a] Defined in the text.
[b] From Ref. [1]

of up to 60 s and in the presence of argon. The only phenomenon observed at long residence times is, as usual, the formation of the hydrogen-bonded adducts $(ROH\cdots OR)^-$.

3. Computational methods

The species examined in this work are of substantial size. This is why calculations were carried out at relatively modest computational levels using ab initio and DFT calculations with the 6-311 + G(d,p) basis set [24]. In all cases the geometries were fully optimized. This provided the electronic-plus-nuclear energies for all the species. Harmonic vibrational frequencies were computed for the structures optimized at the B3LYP/6-311 + G(d,p) level and used for the computation of the zero-point vibrational energies (ZPVE), thermal corrections to the enthalpy (TCEn) and molar entropies, S°_m. The ab initio electronic-plus-nuclear energies for all the species were combined with energies obtained at this level with the ZPVE, TCEn and S°_m obtained in the DFT calculations. Inasmuch as we are not aware of the availability of correcting factors for harmonic frequencies obtained at this level, they were used without scaling. A recent comparison of performances of the various computational methods is available [25].

The raw computational results are given as supporting information in Tables S1 and S2.

A natural bond orbital (NBO) [26] study of orbital interactions was carried out at the MP2/6-311 + G(d,p) level. Atomic charges were calculated using the HF/6-311 + G(d,p) wave functions for the MP2-optimized structures.

In all cases, the Gaussian 03 package [27] was used.

We summarize in Table 3 the experimental gas-phase acidities of six species, ethanol (**1**), *iso*-propanol (**2**), *tert*-butyl alcohol, (**3**) 1-adamantanol (**4**), 2,2,2-trifluoroethanol (**5**), 1,1,1,3,3,3-hexafluoro-2-propanol (**6**), perfluoro-*tert*-butyl alcohol (**7**), and perfluoro1-adamantanol (**8**). These results are compared to the values obtained by means of the DFT and ab initio calculations. Also, some values obtained at the G3 level are reported for comparison purposes. The differences between the experimental and computed *GA* values are given in parentheses.

These results indicate that both DFT and ab initio methods practically perform equally well at giving the *GA* values of non-fluorinated alcohols. In the case of perfluorinated species, both methods are less satisfactory, the MP2 being better. For both methods, the difference between the experimental and computed *GA* values over the range of acidities **6**–**8** remains constant within 4–5 kJ mol^{-1}. This is the range of acidities relevant in this study. For this reason, they both provide reasonably good estimates of differences in acidities. For the purpose of estimating *GA* values for compounds which were not available to us, we anchored the values for non-fluorinated and perfluorinated alcohols ROH respectively to the experimental *GA* values for **3** and **7** through Eqs. (6) and (7), based on isodesmic processes:

$$GA(\text{ROH}) = GA(tert\text{-}C_4H_9OH)_{\text{exp}} + [GA(\text{ROH})_{\text{comp}} - GA(tert\text{-}C_4H_9OH)_{\text{comp}}] \quad (6)$$

$$GA(\text{ROH}) = GA(tert\text{-}C_4F_9OH)_{\text{exp}} + [GA(\text{ROH})_{\text{comp}} - GA(tert\text{-}C_4F_9OH)_{\text{comp}}] \quad (7)$$

4. Experimental and computational results discussion

We summarize in Table 4 the experimental or computed *GA* values determined in this work.

From these data it appears that the acidity of non-fluorinated bridgehead alcohols increases with the internal strain of the parent hydrocarbons (adamantane < bicyclo[2.2.2]octane < norbornane < cubane [28]). This is reminiscent of the influence of internal strain on the stability of bridgehead carbenium ions [29,30].

Given in Table S3 (Supporting Information) are the gas-phase acidities of several aliphatic alcohols (alcohols with long chains are not included because of the possible coiling of the anions

Table 3
Experimental and computed values of *GA*(ROH) for selected alcohols

Alcohol	*GA*(exp)	*GA*(B3LYP)	*GA*(MP2)	*GA*(G3)
C_2H_5OH	1551.4[a]	1544.4 (−7.0)	1558.5 (7.2)	1558.5 (7.1)
i-C_3H_7OH	1543.1[a]	1534.9 (−8.2)	1535.8 (−7.3)	1535.3 (−7.8)
t-C_4H_9OH	1539.7[a]	1534.6 (−5.1)	1541.8 (2.1)	
$C_{10}H_{15}OH$	1530.4[b]	1525.3 (−5.1)	1528.7 (−1.3)	
CF_3CH_2OH	1482.4[a]	1464.6 (−17.8)	1480.2 (−2.2)	1486.0 (3.6)
$(CF_3)_2CHOH$	1416.0[a]	1390.1 (−25.9)	1408.0 (−8.0)	1416.9 (0.9)
t-C_4F_9OH	1355.6[a]	1324.1 (−31.5)	1344.8 (−10.8)	
$C_{10}F_{15}OH$	1320.7[b]	1289.7 (−31.0)	1307.8 (−11.9)	

All values in kJ mol^{-1}. Defined in the text.
[a] Experimental, from Ref. [1].
[b] Experimental, this work.

Table 4
Experimental and computed *GA* values for selected alcohols

Alcohol	*GA* (kJ mol^{-1})
$C_7H_{11}OH$	1519.5[a] (1520.9[b])
$C_8H_{13}OH$	1526.8[a] (1530.1[b])
C_8H_7OH	1472.1[a] (1476.0[b])
1-$C_{10}H_{15}OH$	1530.4[c]
t-C_4F_9OH	1355.6[d]
$C_7F_{11}OH$	1337.8[a] (1339.4[b])
$C_8F_{13}OH$	1332.0[a] (1333.2[b])
C_8F_7OH	1346.5[a] (1354.2[b])
1-$C_{10}F_{15}OH$	1320.7[c]

[a] Computed, ab initio. See text.
[b] Computed, DFT. See text.
[d] Experimental, from Ref. [1].
[c] Experimental, this work.

Table 5
Computed (MP2) C(α)—C(β) and C(α)—O bond lengths

Compound	C(α)—C(β)	C(α)—O
$C_7H_{11}OH$	1.538 (1.540)	1.414 (1.416)
$C_7F_{11}OH$	1.548 (1.563)	1.377 (1.374)
$C_7H_{11}O^-$	1.576 (1.592)	1.326 (1.318)
$C_7F_{11}O^-$	1.5948 (1.621)	1.284 (1.271)
$C_8H_{13}OH$	1.527 (1.534)	1.427 (1.432)
$C_8F_{13}OH$	1.550 (1.566)	1.386 (1.382)
$C_8H_{13}O^-$	1.5632 (1.576)	1.341 (1.336)
$C_8F_{13}O^-$	1.594 (1.620)	1.287 (1.275)
C_8H_7OH	1.574 (1.579)	1.389 (1.387)
C_8F_7OH	1.584 (1.589)	1.368 (1.364)
$C_8H_7O^-$	1.644 (1.645)	1.280 (1.279)
$C_8F_7O^-$	1.663 (1.668)	1.262 (1.256)
$C_{10}H_{15}OH$	1.532 (1.540)	1.430 (1.433)
$C_{10}F_{15}OH$	1.555 (1.572)	1.387 (1.382)
$C_{10}H_{15}O^-$	1.561 (1.575)	1.342 (1.336)
$C_{10}F_{15}O^-$	1.591 (1.602)	1.288 1.275

All values in Å. Values in parentheses were obtained at the B3LYP/6-311 + G(d,p) level.

[31]), and 1-adamantanol together with the polarizability parameters for their hydrocarbon moieties, σ_α. Although differential structural effects on acidities are not large, it can be observed that *GA* does increase with σ_α and 1-adamantanol, as expected, is the most acidic. 1-Norbornyl alcohol is predicted to be substantially more acidic than 1-adamantanol. Cubanol is a very interesting species, expected to be some 70 kJ mol^{-1} more acidic than *tert*-butyl alcohol. Unfortunately, its short shelf life [32] has prevented us from experimentally confirming this high acidity.

Perfluoro1-adamantanol is more acidic than 1-adamantanol and $(CF_3)_3COH$, respectively by 209.7 and 34.9 kJ mol^{-1}. This acidity is thus comparable to that of perfluorinated carboxylic acids (see Table 1) and, to our knowledge, the highest hitherto reported for an alcohol. 1:1 Hydrogen bonding interactions involving neutral species are quite sensitive to steric effects. However, fluorination of aliphatic alcohols is known to override them, both in solution and in the gas phase [32–34]. The ranking of hydrogen bonding donor strength $MeOH \ll CF_3CH_2OH \ll (CF_3)_2CHOH < (CF_3)_3COH$ mirrors the ranking of intrinsic acidities. We thus expect perfluoro1-adamantanol to be stronger than $(CF_3)_3COH$, one of the strongest hydrogen bonding acids known.

Data in Table 4 shows that the ranking of acidities of bridgehead alcohols changes upon fluorination, the ranking being perfluorocubanol < perfluoro1-norbornanol < perfluoro1-bicyclo[2.2.2]octanol < perfluoro1-adamantanol. A possible reason is that perfluorination substantially modifies the internal strain of the hydrocarbon cage (see below).

The NBO study indicates that in all cases, the most important energetic effect in the alcohols and alkoxides studied here is the $n \rightarrow \sigma^*$ charge transfer from the lone pairs on the oxygen to the antibonding C(α)–C(β) σ^* orbitals. This process is associated to a lengthening of the C(α)–C(β) bond. Energetically, its contribution is large. It reaches ca. 166 and 93 kJ mol^{-1}, respectively in $C_{10}F_{15}O^-$ and $C_{10}H_{15}O^-$. For the neutral species, it is generally smaller, 45 and 38 kJ mol^{-1} in $C_{10}F_{15}OH$ and $C_{10}H_{15}OH$, respectively. We collect in Table 5, the computed C(α)–C(β) and C(α)–O distances for the various species studied in this work.

The lengthening of the C(α)–C(β) bond in the anionic forms is significant in all cases and, as indicated above, tends to release part of the internal strain of the hydrocarbon moiety and thus stabilizes the anion (an excessive elongation would produce an "anti-Bredt" destabilization). This helps explain the large acidity of cubanol. For cubane alkoxide anion, the interaction $n \rightarrow \sigma^*$ is also important, 167 kJ mol^{-1}. The energy of this orbital interaction in cubanol amounts to ca. 65 kJ mol^{-1}, a substantial value. In the case of cubylamine, it is even larger, 77 kJ mol^{-1}. The existence of this strong stabilizing stereoelectronic interaction between the amino group and the hydrocarbon moiety, predicted by theoretical means [35], was confirmed experimentally in the gas phase and in solution [36,37]. At variance with cubanol, perfluorocubanol is not significantly more acidic than the other perfluorinated alcohols examined here although the $n \rightarrow \sigma^*$ interaction in its anion, ca. 176 kJ mol^{-1}, is slightly more important than in cubane alkoxide ion. This suggests that perfluorination reduces the strain of the cubic framework of the alcohol. It has been indicated that perfluorination increases the strain energy of cyclopropane and reduces that of cyclobutane [38]. This might originate in a reduction of the aromaticity of cyclopropane and the antiaromaticity of cyclobutane (and cubane) [39]. This and other features indicated earlier, highlight the dire need of reliable thermochemical data for perfluorinated compounds.

From the energetic standpoint, fluorine anionic hyperconjugation seems to have a very modest contribution. A clean example is provided by the anion of perfluoro1-adamantanol. In this species there is a small (ca. 15 kJ mol^{-1}) stabilizing interaction involving the bonding σ orbital C(α)–C(β) and σ^*, the C(γ)–F antibonding one. In the case of 1-adamantanol, the interaction between the σ orbital C(α)–C(β) and σ^*, the C(γ)–H antibonding one, this interaction amounts to ca 13 kJ mol^{-1}. These effects are even smaller in the case of secondary carbons.

These mechanisms of orbital interactions and charge dispersal are stereoelectronic and this is reflected by the geometry of the various species. We present in Table 6 geometrical data for the adamantane derivatives. In the two alcohols, the C(α)OH plane is a plane of symmetry for the molecules. As it can be

Table 6
Computed (ab initio and DFT) bond lengths (in Å) for the adamantane derivatives studied in this work

Compound	C(α)–C(β)	C(β)–C(γ)	C(γ)–C(δ)	C(β)–F	C(γ)–F	C(δ)–F	C(β)–H	C(γ)–H	C(δ)–H	C(α)–O
$C_{10}H_{15}OH$	1.532[a]	1.537[a]	1.536[a]	–	–	–	1.101[a]	1.098[a]	1.098[a]	1.430[b]
	1.526[b]	1.537[b]	1.537[b]	–	–	–	1.098[b]	1.097[b]	1.098[b]	1.430[b]
	(1.540)[a]	(1.543)[a]	(1.543)[a]	–	–	–	(1.098)	(1.095)[a]	(1.096)[a]	(1.433)[b]
	(1.535)[b]	(1.542)[b]	(1.542)[b]	–	–	–	(1.095)[b]	(1.095)[b]	(1.096)[b]	(1.433)[b]
$C_{10}F_{15}OH$	1.555[a]	1.545[a]	1.549[a]	1.343[a,c]; 1.355[a,d]	1.359[a]	1.344[a,c]; 1.345[a,d]				1.387[b]
	1.550[b]	1.553[b]	1.549[b]	1.345[b,c], 1.345[b,c]	1.358[b]	1.344[b,c]; 1.345[b,c]				1.387[b]
	(1.571)[a]	(1.558)[a]	(1.564)[a]	(1.347[c])[a]; (1.359[d])[a]	(1.360)[a]	(1.348[c])[a]; (1.348[d])[a]				(1.382)[b]
	(1.565)[b]	(1.568)[b]	(1.564)[b]	(1.348[c])[b]; (1.348[d])[b]	(1.359)[b]	(1.348[c])[b]; (1.349[d])[b]				(1.382)[b]
$C_{10}H_{15}O^-$	1.561	1.537	1.536	–	–	–	1.100	1.103	1.103	1.342
	(1.575)	(1.544)	(1.542)	–	–	–	(1.097)	(1.101)	(1.100)	(1.336)
$C_{10}F_{15}O^-$	1.591	1.547	1.543	1.356[c]; 1.356[d]	1.372	1.348[c]; 1.358[d]	–	–	–	1.288
	(1.620)	(1.559)	(1.558)	(1.360[c]); (1.360[d])	(1.376)	(1.352[c]); (1.361[d])	–	–	–	(1.275)

MP2/6-311 + G^{**} and (B3LYP/6-311 + G^{**}) results.

[a] Carbons C(β) and C(δ) out of the plane of symmetry of the molecule.

[b] Carbons C(α), C(β) and C(δ) in the plane of symmetry of the molecule.

[c] Equatorial position in the six-membered ring.

[d] Axial position in the six-membered ring.

seen in the table, bond lengths are slightly different for bonds in and out of the plane.

5. Conclusions

1. Perfluoro1-adamantanol is the most acidic alcohol reported to date.
2. The intrinsic acidity of non-fluorinated bridgehead alcohols increases with the strain of the hydrocarbon framework.
3. Perfluorination of these compounds strongly increases their acidity.
4. Perfluorination modifies the molecule's internal strain such that the relative ordering of acidity found for the parent compounds differs from that of the perfluorinated compounds.
5. A natural bond orbitals (NBO) analysis indicates that the most important energetic effect in the alcohols and alkoxides studied here is the $n \rightarrow \sigma^*$ charge transfer from the lone pairs on the oxygen to the antibonding C(α)–C(β) σ^* orbitals. The quantitative effect of the anionic fluorine hyperconjugation is significantly smaller.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2007.02.056.

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