Proc. Estonian Acad. Sci. Chem., 2005, **54**, 2, 60–69

The pervasive influence of hyperconjugation: the intrinsic (gas phase) acidities of adamantane, adamantanol, and some of their fluorinated derivatives

Dedicated to Professor I. A. Koppel on his 65th birthday

José-Luis M. Abboud[a, c*], Masaaki Mishima[a], and Takaaki Sonoda[b]

[a] Kyushu University, Institute of Materials Chemistry and Engineering, Higashi-ku, 6-10-1 Hakozaki, Fukuoka 8128581, Japan; mishima@ms.ifoc.kyushu-u.ac.jp
[b] Kyushu University, Institute of Materials Chemistry and Engineering, Kasuga, Fukuoka 8168580, Japan; sonoda@cm.kyushu-u.ac.jp
[c] Permanent address: Instituto de Química Física Rocasolano, CSIC. C/ Serrano 119, E-28006, Madrid, Spain

Received 26 January 2005, in revised form 7 March 2005

Abstract. In this work the results of a computational study at the B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) level of the title compounds, the conjugated bases derived therefrom, and some ancillary compounds are reported. The most significant conclusions drawn are (i) that 1-H perfluoroadamantane and perfluoro-1-adamantanol are expected to be endowed with an intrinsic gas phase acidity close to 310 kcal mol^{-1}, similar to that of strong conventional acids such as trifluoroacetic or methane sulphonic acids, and (ii) hyperconjugative effects on the structures of these species and their corresponding anions are seen to be quite significant although their detailed dissection remains a topic for future studies.

Key words: gas phase acidity, 1-H-perfluoroadamantane, perfluoro-1-adamantanol, DFT calculations, hyperconjugation.

INTRODUCTION

We have been involved for some time in the study of structural effects on the thermodynamic stability, acidity, and basicity of molecules and ions both in the

* Corresponding author, jlabboud@iqfr.csic.es

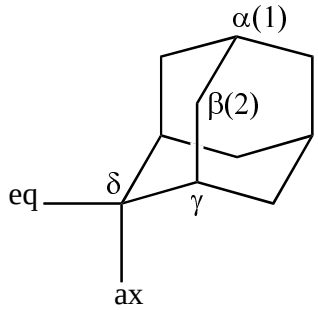

Fig. 1. Labelling of the adamantane framework.

gas phase and in solution [1–4]. Nowadays, an important challenge is the quest for strong and super-strong acids and bases [5–8]. This is a significant scientific target with far-reaching industrial applications, particularly in the cases where the conjugate bases have weak coordinating powers [9–11].

The aim of this work is to contribute to current investigations in the field of the relationships between the structure and intrinsic (gas phase) acidity of neutral species. In particular, and because of our ongoing studies on carbanionic species [12–14], we are interested in the stability of the carbanions derived from adamantane (Fig. 1) and substituted adamantanes. 1-Adamantyl is an important alicyclic group. Its parent compound, adamantane hydrocarbon, is a stable, highly symmetric molecule (T_d) with small internal strain. 1-Adamantyl cations are "protected" by Bredt's effect [15–16]. Interestingly, 2-adamantyl cation is a "non-classical" ion [17].

For comparison purposes, we have also studied the intrinsic acidity of 1-adamantanol and perfluoro-1H-adamantanol.

In the Taft-Topsom formalism (see, e.g. [18]), designed for the study of gas phase reactivity, the 1-adamantyl group appears as endowed with a very large polarizability (as measured by the polarizability parameter σ_α) but with very small resonance and field capabilities. As we shall discuss below, the large polarizability of the 1-adamantyl substituent plays an important role in the gas phase- and even solution reactivity of species in which it is involved as a substituent.

The present study is purely computational and it is intended to pave the way for future experimental work.

QUANTITATIVE APPROACH AND COMPUTATIONAL METHODS

Calculations were performed at the B3LYP/6-311+G(d,p) level using the Gaussian 98 package of computer programs [19]. The raw results obtained in this work are presented in Table 1. The reported ZPVE values are not scaled. Entropy values at 298.15 K, S^0_{298} can be derived from the values of H_{298} and G_{298} by

Table 1. Summary of the computational results obtained in this work[a, b]

Species	E	ZPVE	H_{298}	G_{298}
Adamantane	−390.824417	0.243378	−390.573251	−390.609383
1-Adamantanide anion	−390.143789	0.223832	−389.919957	−389.957889
1H-perfluoroadamantane (**1**-H)	−1879.798846	0.117666	−1879.660768	−1879.724172
1H-perfluoroadamantanide anion (**1**$^-$)	−1879.251147	0.102663	−1879.147540	−1879.211966
1-Adamantanol (**2**-H)	−466.062679	0.246012	−465.816667	−465.858098
1-Adamantanoxide anion (**2**$^-$)	−465.457614	0.230255	−465.227359	−465.267120
Perfluoro-1-adamantanol (**3**-H)	−1955.030765	0.121061	−1954.887879	−1954.954849
Perfluoro-1-adamantanoxide anion (**3**$^-$)	−1954.516191	0.106759	−1954.388701	−1954.453544
Methane	−40.533983	0.044596	−40.486518	−40.528442
Methanide anion	−39.8559538	0.028508	−39.824513	−39.868122
Isobutane	−158.5064496	0.130607	−158.370000	−158.438683
tert-Butanide anion	−157.8371049	0.113264	−157.718327	−157.785728
tert-Butyl alcohol	−233.752405	0.135080	−233.610659	−233.647165
tert-Butoxide anion	−233.143783	0.119442231	−233.017877	−233.059878

[a] At the B3LYP/6-311+G(d,p) level.
[b] All values in Hartree.

considering that $S^0_{298} = (\mathrm{H}_{298} - \mathrm{G}_{298})/T$ and $T = 298.15$ K. These data allow us to compute the gas phase acidity of the various neutral species and the proton affinities (PA) of their conjugate (anionic) bases. In the general case of a protic acid H-A in the gas phase, these properties are defined by means of reaction 1:

$$\text{H-A(g)} \rightarrow \mathrm{A^-(g)} + \mathrm{H^+(g)} \qquad \Delta G^0_{\mathrm{ac}}(\mathrm{HA}), \Delta_{\mathrm{r}} H^0_{\mathrm{m}}(1), \tag{1}$$

where, by definition, $\mathrm{PA(A^-)} = \Delta_{\mathrm{r}} H^0_{\mathrm{m}}(1)$ while $\Delta G^0_{\mathrm{ac}}(\mathrm{HA})$ is known as the gas phase acidity of H-A.

The computational level of this work is relatively modest. This is due to the very large size of some of the species examined herein. For instance, perfluoro-1-adamantanol at this level requires 578 basis functions. In order to allow a more accurate discussion, instead of directly using the absolute PA or ΔG^0_{ac} values defined by Eq. 1, we shall use $\Delta\mathrm{PA}$ (relative proton affinities) or $\Delta\Delta G^0_{\mathrm{ac}}$ (relative gas phase acidities) values defined through the isodesmic reaction 2.

$$\text{H-A(g)} + \mathrm{A^-_{ref}(g)} \rightarrow \mathrm{A^-(g)} + \text{H-A}_{\mathrm{ref}}\text{(g)} \qquad \Delta\Delta G^0_{\mathrm{ac}}(\mathrm{HA}), \Delta\Delta_{\mathrm{r}} H^0_{\mathrm{m}}(2), \tag{2}$$

where $\text{H-A}_{\mathrm{ref}}$ is a reference acid for which experimental values of ΔG^0_{ac} and/or $\mathrm{PA(A^-)}$ are available. For instance, in the case of adamantane (AdH), isobutane is a convenient reference for the computational estimate of the PA of 1-adamantanide anion (1-Ad$^-$). Then, Eq. 3 applies.

$$\mathrm{AdH(g)} + \textit{tert}\text{-}\mathrm{C_4H_9^-(g)} \rightarrow \text{1-Ad}^-\mathrm{(g)} + \textit{iso}\text{-}\mathrm{C_4H_{10}(g)} \quad \Delta\Delta G^0_{\mathrm{ac}}(\mathrm{HA}), \Delta\Delta_{\mathrm{r}} H^0_{\mathrm{m}}(3) \tag{3}$$

Table 2. Pertaining to the computed relative gas phase acidities of selected compounds[a, b]

Compound	Reference	$\Delta\Delta G^0_{ac}$ (H-A)	PA(A^-)
Adamantane	Isobutane	−0.9 (405.7 ± 2.1)[c]	1.0 (413.1 ± 2.0)[d]
1-H	1H-adamantane	−87.4 (404.8)[c]	−87.9 (414.1)[d]
2-H	*tert*-Butanol	−2.4 (368.1 ± 1.1)[c]	−1.5 (374.7 ± 1.0)[d]
3-H	1-Adamantanol	−56.7 (365.7)[c]	−56.3 (372.8)[d]

[a] This work.
[b] All values in kcal mol^{-1}.
[c] ΔG^0_{ac} (H-A_{ref}).
[d] PA(A^-_{ref}).

This equation defines a scale of *relative* acidities referred to isobutane. *Absolute* values, as defined by Eq. 1 can be obtained by means of the experimental data for the reference compound. Other references have been used as appropriate. The computed relative gas phase acidities and proton affinities obtained in the present study are summarized in Table 2.

STRUCTURAL EFFECTS ON THE INTRINSIC ACIDITIES AND MOLECULAR GEOMETRIES OF ADAMANTANE, 1-ADAMANTANOL, 1-H PERFLUOROADAMANTANE, AND PERFLUORO-1-ADAMANTANOL AND THEIR CORRESPONDING ANIONS

The intrinsic acidities of these compounds, as defined through Eq. 1 and calculated as indicated above, are summarized in Table 3. Also, for comparison purposes, we give in this Table experimental and computed data for other compounds. The latter, recently obtained at the G2 level, are known to agree within 1 kcal mol^{-1} with the experimental values.

The influence of factors affecting the thermodynamic stability of the various species examined herein is also mirrored by modifications of bond lengths. Table 4 summarizes bond lengths important for the present discussion.

Table 3. Experimental and calculated $\Delta G^0_{ac}(HA)$ and $PA(A^-)$ values relevant to this study

Compound (A-H)	$\Delta G^0_{ac}(HA)$	$PA(A^-)$
CH_4[a]	410.1	418.4
C_2H_6[a]	411.9	420.6
C_3H_8[a]	408.5	416.5
iso-C_4H_{10}[a]	404.7	412.2
c-C_3H_6[a]	404.6	413.4
c-C_4H_8[a]	406.4	414.7
c-C_5H_{10}[a]	406.1	411.8
c-C_6H_{12}[a]	403.7	413.7
1H-adamantane[b]	404.8	414.1
Perfluoroisobutane[c]	326.6 ± 2.0	334.3 ± 2.1
1H-undecafluorobicyclo[2.2.1]heptane[c]	334.4 ± 2.0	342.1 ± 2.1
1H-perfluoroadamantane[b]	317.4	326.2
Methanol[d]	375.1 ± 1.0	382.0 ± 1.0
Ethanol[d]	371.7 ± 1.0	378.3 ± 1.0
iso-Propanol[d]	368.5 ± 1.0	375.5 ± 1.0
tert-Butanol[d]	368.1 ± 1.0	374.7 ± 1.0
1-Adamantanol[b]	365.7	372.8
Perfluoro-*tert*-butanol[d]	324.0 ± 2.0	331.6 ± 2.2
1H-perfluoroadamantanol[b]	309.0	316.5

[a] At the G2 level(4).
[b] At the B3LYP/6-311+G(d,p) level. This work.
[c] Experimental value(14).
[d] From [30].

Table 4. Summary of bond lengths in some species examined in this study[a]

Compound	C(α)–C(β)	C(β)–C(γ)	C(γ)–C(δ)	C(β)–F	C(γ)-F	C(δ)-F
$C_{10}H_{16}$	1.543	1.543	1.543	–	–	–
$C_{10}H_{15}^-$	1.525	1.558	1.543	–	–	–
$C_{10}F_{15}H$	1.550	1.563	1.565	1.353	1.359	1.348[b], 1.348[c]
$C_{10}F_{15}^-$	1.498	1.570	1.561	1.373	1.384	1.363[b], 1.357[c]
$C_{10}H_{15}OH$	1.541[d]	1.544[d]	1.543[d]			
	1.535[e]	1.543[e]	1.542[e]			
$C_{10}H_{15}O^-$	1.575	1.544	1.542			
$C_{10}F_{15}OH$	1.572[d]	1.559[d]	1.564[d]	1.358[d], 1.347 [d]	1.360[d]	1.348[b, d]; 1.349[c, d]
	1.565[e]	1.569[e]	1.565[e]	1.348[e]	1.359[e]	1.348[b, e]; 1.347[c, e]
$C_{10}F_{15}O^-$	1.620	1.560	1.558	1.360, 1.360	1.376	1.361[b], 1.352[c]

[a] All values in angstrom.
[b] Equatorial position in the six-membered ring.
[c] Axial position in the six-membered ring.
[d] Carbons C(β) and C(γ) outside the plane of symmetry of the molecule.
[e] Carbons C(α), C(β), and C(γ) in the plane of symmetry of the molecule.

The cases of adamantane and 1H-perfluoroadamantane

From the data gathered in Table 3 it is clear that the intrinsic gas phase acidity of the hydrogen attached to the tertiary carbon in position 1 is quite similar to that of the hydrogens borne by the secondary and tertiary carbons in a variety of aliphatic and alicyclic hydrocarbons. It is interesting that the polarizabilities (as defined by Taft & Topsom [7]) of the hydrocarbon moieties in these compounds span a substantial range. However, at variance with the most general case, these acidities do not seem to directly reflect differences in polarizability. This result is consistent with the concept that the stabilization of aliphatic and alicyclic carbanions is largely dependent on anionic hyperconjugation, involving the interaction between the electronic "lone pair" and antibonding C–H and C–C σ^* orbitals β to the anionic centre [20–24]. The importance of this interaction, previously substantiated in a number of cases by NBO calculations [20, 21], is responsible for the lengthening predicted for the C(β)–C(γ) bond (see Table 4). We also observe a contraction of the C(α)–C(β) bond. This effect, formally "anti-Bredt", possibly reflects a stabilizing interaction between the "lone pair" and a bonding π orbital between C(α) and C(β). This possibility is currently being explored by means of the NBO method.

In the case of **1**H, the effect of perfluorination on acidity is extremely large. Thus, this compound is predicted to display an intrinsic acidity comparable to that of trifluoroacetic or methane sulphonic acids (see Table 3). As regards the effect of perfluorination on the geometries of **1**H and its conjugate base, $\mathbf{1}^-$, the following is observed:

In **1**H there is a general lengthening of all C–C distances suggesting the action of the electron-withdrawing effect of the fluorine substituents.

The bond lengths of **1**H and $\mathbf{1}^-$ are expected to be affected by two main factors [25]: (i) the influence of fluorine on the relative energies of the various bonding and atibonding C–C and C–F orbitals, and (ii) the possible intervention of fluorine hyperconjugation. The pattern of C–C distances is quite similar to that of 1-adamantanide anion. Some important differences are as follows: (i) The "anti-Bredt" contraction of the C(α)–C(β) bond is quite significant here. (ii) The C(β)–C(γ) bond is longer here than in the case of **1**H but the differential effect is smaller than that observed in the couple adamantane/adamantanide anion. (iii) The C(γ)–C(δ) bond length is very slightly shorter in $\mathbf{1}^-$ than in 1H. The differences in C–F distances between **1**H and $\mathbf{1}^-$ are modest but nevertheless significant. Without exception, they are longer in $\mathbf{1}^-$ than in **1**H. This tends to suggest fluorine hyperconjugation with a transfer of electron density from the σ(C–C) orbitals to the σ^*(C–F) ones. Furthermore, as indicated by the two different C(δ)–F distances, the effect has a significant stereoelectronic character, a feature fully consistent with hyperconjugation.

The cases of 1-adamantanol (2H) and perfluoro-1-adamantanol (3H)

The calculated gas phase acidity value (as defined through Eq. 1) of **2**H is 372.8 kcal mol^{-1}, slightly smaller than that of *tert*-butanol. This result is consistent with the polarizabilities of *tert*-butyl and 1-adamantyl, respectively –0.75 and –0.95, and with the known linear dependence of gas phase acidities of alcohols with substituent polarizabilities.

Notice that the molecule **2**H belongs to the C_s symmetry point group. This originates in the fact that the plane is defined by C(α) and the OH group is also a symmetry plane for the molecule. Interestingly, this is reflected in the various C–C bond lengths. It is noteworthy that in the case wherein both C(β) and C(γ) are in the symmetry plane, the C(α)–C(β) bond is shorter than for the other two (symmetrical) bonds. Although the effect is small, it is significant because it indicates an electronic transfer from the lone pairs of oxygen to the two C(α)–C(β) bonds best oriented for the stereoelectronic charge transfer.

The gas phase acidity value (as defined according to Eq. 1) of **3**H is quite close to that of **1**H. This seems surprising because to our knowledge, alcohols are consistently much more acidic than the parent hydrocarbons. Notice, however, that multiple fluorine substitution deeply affects the relative gas phase acidities of neutral acids. More precisely, computational studies have shown that successive α-fluorination strongly reduces the gap between the acidities of alcohols and thiols [26].

Examination of the bond lengths in **3**H reveals that the pattern of C–C distances is similar to that of **1**H but the lengthening is much more important, comparable to or even larger than that found in **1**$^-$. On the other hand, the various C–F bonds have lengths very close to those found in **1**H. These results seem to indicate that in **3**H, the electron donation from the oxygen to the hydrocarbon framework is important (possibly as a consequence of the perturbation of the energies of bonding and antibonding C–C orbitals under the influence of substitution by fluorine) but the importance of fluorine hyperconjugation *seems* small. In the case of **3**$^-$, the lengthening of the C(α)–C(β) bond reaches nearly 0.7 angstrom. This *seems* to indicate an important weakening of this bond and, likely, an increase of the internal strain in the hydrocarbon framework. Some time ago, Koppel and co-workers explained the low acidity of 1H-undecafluoro-bicyclo[2.2.1]heptane relative to perfluoroisobutane on the basis of the fluorine hyperconjugation being blocked by Bredt's effect in the case of the cyclic anion [27]. Here, even though Bredt's rule is not formally violated, the situation is similar, as considerable strain is introduced. Quite interestingly, the C–F bonds are less stretched on going from **3**H to **3**$^-$ than on going from **1**H to **1**$^-$. Likely, here further electron withdrawing from the stretched C–C bonds would increase the destabilization of the ion.

The results presented above for **3**H and **3**$^-$ are certainly complex. In fact, while the effect of fluorine substitution on bond lengths and likely also on bond energies or IR stretching frequencies of the appropriate oscillators (e.g., C–F

bonds) can often be rationalized in terms of the σ(C–C) → σ*(C–F) intramolecular charge transfer (for a recent important example involving fluorine–graphite intercalation compounds (fluorine–CGICs), see [28]), recent computational studies clearly reveal that other intramolecular charge shifts formally associated to hyperconjugation are relevant in terms of energetic contributions. More important yet, bond lengthening does not necessarily imply a destabilization of the molecule (or ion) [29]. Under these conditions, our results ought to be considered as a very preliminary approach to the problem of structural effects attending perfluorination of the 1-adamantyl framework.

CONCLUSIONS

1-H perfluoroadamantane and perfluoro-1-adamantanol are predicted to be endowed with an intrinsic gas phase acidity close to 310 kcal mol^{-1}, similar to that of strong conventional acids such as trifluoroacetic or methane sulphonic acids. Hyperconjugative effects on the structures of these species and their corresponding anions are seen to be quite significant although their detailed dissection remains a topic for future studies.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan, and by the Spanish DGES Project BQU2003-05827.

REFERENCES

1. Abboud, J.-L. M., Alkorta, I., Burk, P., Dávalos, J. Z., Quintanilla, E., Della, E. W., Koppel, I. A. & Koppel, I. The enormous apparent gas-phase acidity of cubylamine. *Chem. Phys. Lett.*, 2004, **398**, 560–563.
2. Abboud, J.-L. M., Koppel, I. A., Alkorta, I., Della, E. W., Müller, P., Dávalos, J. Z., Burk, P., Koppel, I., Quintanilla, E., & Pihl, V. Stereoelectronic, strain and medium effects on the protonation of cubylamine, a Janus-like base. *Angew. Chem. Int. Ed*., 2003, **42**, 2281–2285.
3. Abboud, J.-L. M., Alkorta, I., Dávalos, J. Z., Müller, P. & Quintanilla, E. Thermodynamic stabilities of carbenium ions. *Adv. Phys. Org. Chem*., 2002, **37**, 57–135.
4. Takeuchi, K., Takasuka, M., Shiba, E., Kinoshita, T., Okazaki, T., Abboud, J.-L. M., Notario, R. & Castaño, O. Experimental and theoretical evaluation of energetics for nucleophilic solvent participation in the solvolysis of tertiary alkyl chlorides on the basis of gas phase bridgehead carbocation stabilities. *J. Am. Chem. Soc*., 2000, **122**, 7351–7357.
5. Kaljurand, I., Rodima, T., Pihl, A., Mäemets, V., Leito, I., Koppel, I. A. & Mishima, M. Acid-base equilibria in nonpolar media. 4. Extension of the self-consistent basicity scale in THF medium. Gas-phase basicities of phosphazenes. *J. Org. Chem*., 2003, **86**, 9988–9993.
6. Yagupolskii, L. M., Petrik, V. N., Kondratenko, N. V., Sooväli, L., Kaljurand, I., Leito, I. & Koppel, I. A. The immense acidifying effect of the supersubstituent $=NSO_2CF_3$ on the

acidity of amides and amidines of benzoic acids in acetonitrile. *J. Chem. Soc. Perkin Trans. 2*, 2002, 1950–1955.
7. Koppel, I. A., Burk, P., Koppel, I. & Leito, I. Generalized principle of designing neutral superstrong Brønsted acids. *J. Am. Chem. Soc.*, 2002, **124**, 5594–5600.
8. Koppel, I. A., Leito, I., Mishima, M. & Yagupolskii, L. M. The enormous acidifying effect of the supersubstituent = NSO_2CF_3 on the acidity of derivatives of benzenesulfonamide and toluene-*p*-sulfonamide in the gas phase and in dimethyl sulfoxide. *J. Chem. Soc. Perkin Trans. 2*, 2001, 229–232.
9. Hong, E. S., Okada, S., Sonoda, T., Gopukumar, S. & Yamaki, Y. Thermal stability of electrolytes with mixtures of $LiPF_6$ and $LiBF_4$ used in lithium-ion cells. *J. Electrochem. Soc.*, 2004, **151**, A1836–A1840.
10. Kawamura, T., Sonoda, T., Okada, S. & Yamaki, Y. Improvement of the stability of $LiPF_6$ electrolytes toward water by the addition of LiCl. *Electrochemistry*, 2003, **71**, 1139–1141.
11. Liu, D. F., Liu, J., Zhuo, L. M., Liu, L. W. & Sonoda, T. New type of lithium poly(polyfluoroalkoxy)sulfonylimides as salts for PEO-based solvent-free electrolytes. *J. Appl. Polym. Sci*., 2001, **82**, 1882–1885.
12. Mishima, M., Matsuoka, M., Lei, Y. X. & Rappoport, Z. Gas-phase acidities of disubstituted methanes and of enols of carboxamides substituted by electron-withdrawing groups. *J. Org. Chem.*, 2004, **69**, 5947–5965.
13. Quintanilla, E., Dávalos, J. Z., Abboud, J.-L. M. & Alkorta, I. In *The Chemistry of Cyclobutanes. The Chemistry of Functional Groups* (Rappoport, Z. & Liebman, J. F., eds.). Wiley, Chichester, 2005. Chapter 5.
14. Quintanilla, E., Dávalos, J. Z., Herrero, R., Jiménez, P., Alkorta, I. & Abboud, J.-L. M. Protic acidity of some aliphatic and alicyclic hydrocarbons in the gas phase and in solution. An empirical and computational link. *Collect. Czech. Chem. Commun*., 2004, **69**, 2134–2146.
15. Müller, P. Glossary of terms used in physical organic chemistry. *Pure Appl. Chem.*, 1994, **66**, 1077–1184.
16. Bredt, J. Über sterische Hinderung in Brückenringen (Bredtsche Regel) und über die *meso-trans* Stellung in kondensierten Ryngsystemen des Hexamethylens. *Justus Liebigs Ann. Chem.*, 1924, **437**, 1–13.
17. Abboud, J.-L. M., Alkorta, I. & Dávalos, J. Z. Large structural effects in neutral and protonated species: a computational study. *J. Phys. Org. Chem.*, 2001, **14**, 839–845 and references therein.
18. Hansch, C., Leo, A. & Taft, R. W. A survey of Hammet substituent constants and resonance and field parameters. *Chem. Rev*., 1991, **91**, 165–195.
19. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Zakrzewski, V. G., Montgomery, J. A. Jr., Stratmann, R. E., Burant, J. C., Dapprich, S., Millam, J. M., Daniels, A. D., Kudin, K. N., Strain, M. C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G. A., Ayala, P. Y., Cui, Q., Morokuma, K., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J. B., Cioslowski, J., Ortiz, J. V., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., González, C., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Andrés, J. L., González, C., Head-Gordon, M., Replogle, E. S. & Pople, J. A. *Package Gaussian 98, Revision A.7*. Gaussian, Inc., Pittsburgh PA, 1998.
20. Sauers, R. R. A computational study of proton and electron affinities. *Tetrahedron*, 1999, **55**, 10013–10026.
21. Alkorta, I. & Elguero, J. Carbon acidity and ring strain: A hybrid HF-DFT approach (Becke3LYP/6-311++G**). *Tetrahedron*, 1997, **53**, 9741–9744.
22. Forsyth, D. A. & Yang, J.-R. Intrinsic and equilibrium NMR isotope shift evidence for negative hyperconjugation. *J. Am. Chem. Soc*., 1986, **108**, 2157–2162.
23. Schleyer, P. v. R & Kos, A. The importance of negative (anionic) hyperconjugation. *Tetrahedron*, 1983, **39**, 1141–1144.

24. Pross, A., DeFrees, D. J., Levy, B. A., Pollack, S. K., Radom, L. & Hehre, W. J. Theoretical approach to substituent effects – structures and stabilities of carbanions XCH_2. *J. Org. Chem.*, 1981, **46**, 1693–1700.
25. Hoffmann, R., Radom, L., Pople, J. A., Schleyer, P. v. R., Hehre, W. J. & Salem, L. Strong conformational consequences of hyperconjugation. *J. Am. Chem. Soc.*, 1972, **94**, 6221–6223.
26. Burk, P., Koppel, I. A., Rummel, A. & Trummal, A. Can O–H acid be more acidic than its S–H analog? A G2 study of fluoromethanols and fluoromethanethiols. *J. Phys. Chem. A*, 2000, **104**, 1602–1607.
27. Koppel, I. A., Koppel, J., Pihl, V., Anvia, F. & Taft, R. W. Thermodynamic acidity of $(CF_3)_3CH$ and 1H-undecafluoro bicyclo[2.2.1]heptane. – The concept of anionic (fluorine) hyperconjugation. *J. Am. Chem. Soc.*, 1994, **116**, 8654–8657.
28. Sato, Y., Itoh, K., Higawara, R., Fukunaga, T. & Ito, Y. On the so-called "semi-ionic" C–F bond character in fluorine–GIC. *Carbon*, 2004, **42**, 3243–3249.
29. Kaupp, M. & Riedel, S. On the lack of correlation between bond lengths, dissociation energies and force constants: the fluorine-substituted ethane homologues. *Inorg. Chim. Acta*, 2004, **357**, 1865–1872.
30. Bartmess, J. E. Negative ion energetics data. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69* (Linstrom, P. J. & Mallard, W. G., eds.). March 2003, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).

Hüperkonjugatsiooni kõikjale tungiv mõju: adamantaani, adamantanooli ja nende mõningate fluoroderivaatide gaasifaasilised happelisused

José-Luis M. Abboud, Masaaki Mishima ja Takaaki Sonoda

On esitatud kvantkeemiliste arvutuste abil B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) tasemel saadud andmed adamantaani, adamantanooli ja nende mõningate fluoroderivaatide ning vastavate konjugeeritud aluste kohta. Lisaks on uuritud mõningaid lähedasi ühendeid. Olulisemad järeldused: 1-H-perfluoroadamantaani ja perfluoro-1-adamantanooli oodatavad gaasifaasilised happelisused asuvad 310 kcal mol^{-1} kandis, mis on lähedane tugevatele hapetele (*à la* trifluoroäädikhape, metaansulfoonhape); hüperkonjugatsiooni mõju nende ainete ja vastavate konjugeeritud aluste struktuurile on märkimisväärne, kuid selle detailsem lahkamine vajab lisauuringuid.