The Gas Phase Acidity of Oligofluorobenzenes and Oligochlorobenzenes: About the Additivity or Non-Additivity of Substituent Effects

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Abstract: The deprotonation energies of benzene, fluorobenzene, all di-, tri-, and tetrafluorobenzenes, pentafluorobenzene, chlorobenzene, all di-, tri-, and tetrachlorobenzenes, and pentachlorobenzene have been calculated at various levels of second-order Møller–Plesset and density functional theory. Taking the previously determined experimental data as a benchmark, good agreement was achieved in the chloro series even with moderate computational effort, whereas more extended basis sets have to be used to obtain meaningful numbers in the fluoro series. Apparently, most extensive electron correlation is required to avoid artifacts caused by the proximity of nonbonding lone pairs at the carbanionic center and at the fluorine atoms. When two or more fluorine substituents were introduced in the same aromatic ring, their individual effects (as defined by position-dependent acidity increments) proved to be perfectly additive in the entire series. In contrast, the acidifying effect of chloro substituents was found to level off when the number of such halogens increases. Additivity or non-additivity of element effects cannot be ascertained after having merely compared the acidity of mono- and disubstituted substrates, but only after having moved to higher degrees of substitution.

Keywords: ab initio calculations · additivity · arenes · halogens · substituent effects

Introduction

Chemists tend to parametrize the reactivity of a family of substrates by taking that of the parent compound as the reference and to correct it by considering any substituent effect as a perturbation. This approach will fail if two or more substituents intervene simultaneously unless each of them deploys its action completely uninfluenced by the others. The present work was undertaken to probe the additivity or non-additivity of halogen substituents on the proton affinity of the phenyl anion, a mechanistic key reference.

Organometallic deprotonation and subsequent electrophilic trapping is a powerful method for the derivatization and, in particular, functionalization of arenes and heterocycles.[1–3] Although the crucial hydrogen/metal permutation ("metalation") step normally occurs irreversibly ("under kinetic control"), the knowledge of substituent effects on the equilibrium ("thermodynamically controlled") acidity is of practical use as it helps to find adequate reaction conditions and to rationalize regioselectivity. Moreover, acidity in general and in the arene series in particular is of fundamental importance as a stringent test of whatever theoretical model by juxtaposing its predictions and the experimental reality.

Fluorine is the smallest metalation-promoting substituent. We have determined the gas-phase acidity of fluorobenzene, of all three difluorobenzenes, trifluorobenzenes, and tetrafluorobenzenes and of pentafluorobenzene relative to the parent compound benzene using a Fourier transform ion cyclotron resonance spectrometer.[4] Subsequently we extended this study to mono-, di-, tri-, tetra-, and pentachlorobenzenes.[5] However, the experimental gas-phase methods[6]

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suffer from shortcomings. On one hand, they are not very accurate, standard deviations of up to 2 or 3, even 4 kcal mol^{-1} being not uncommon.[6,7] On the other hand, the acid/base equilibration between two neutral species and the respective anions allows one to directly monitor just the least basic of several species, for example *ortho*-fluorobenzenide upon deprotonation of fluorobenzene or 2,3,6-trifluorobenzenide from 1,2,4-trifluorobenzene. To assess the *meta* and *para* isomers[8] one has to rely on the silane-cleavage technique[9] or another kinetic method which may not always be free of artifacts. Under such circumstances quantum-chemical calculations may provide a more complete picture and, possibly, be more accurate.

Results

When applying the same MP2/6–311+G* method which had proven appropriate in the chlorobenzene series[5] to mono-, di-, tri-, tetra-, and pentafluorobenzenes, the coincidence with the experimental data was found to be poor. Although the numbers mirrored the correct trend, the computation overestimated the experimental acidity differences by about 30% as a comparison between the fluorobenzene/pentafluorobenzene acidity spans of 40.3 versus 30.4 kcal mol^{-1} reveals (Table 1). Apparently, the proximity of all the nonbonding ("lone pair") electrons at the carbanionic center and at the fluorine atoms causes complications. An accurate account for basis set deficiencies and for electron-correlation effects should help to overcome them. The replacement of the 6–311+G* basis set by the cc-pVTZ and finally the aug-cc-pVTZ basis sets as well as the use of the density functional B3LYP method[10] and the recently developed SCS-MP2 approach[11a,b] indeed improved the results considerably. The mean absolute errors diminished from 6.5 over 4.9 and 2.0 to 1.5 and 0.8 kcal mol^{-1} (Table 1).

These results underscore the necessity of employing extended basis sets placing diffuse functions on *all* atoms (e.g., aug-cc-pVTZ versus cc-pVTZ) for the calculation of the deprotonation energies with high accuracy. Allowing for polarization and diffuse functions only on selected atoms as in the initial MP2/6–311+G*//RHF/6–311+G* treatment produces an unbalanced energetic description, especially for anions bearing several fluorine atoms. As the computational deviations increase with the number of halogen substituents such a basis set is obviously not saturated enough. Presumably the imperfections are due to an inadequate description of the fluorine lone pairs. The new SCS-MP2 method[11] unequivocally improves the results as compared to the standard MP2 reference (Table 1). The use of B3LYP rather than Hartree–Fock geometries, in particular in combination with the aug-cc-pVTZ basis proved to be a decisive step towards the calculation of gas-phase deprotonation energies with high accuracy (Table 1). Thus, the B3LYP method has once more been confirmed to be a viable alternative to the computationally more costly perturbation theory treatments.

We have revisited the chlorobenzene series and have recalculated the deprotonation enthalpies using the extended basis sets. The fit with the experimental data ameliorated again, the smallest mean absolute errors being 1.5 and 1.6 kcal mol^{-1} (Table 2).

The deprotonation enthalpies in the chloro series calculated with the SCS-MP2 method are systematically larger than the results obtained with the MP2 and B3LYP methods (Table 2). This is puzzling because to date, in a great variety of situations, the accuracy of the SCS-MP2 method has never fallen behind that of MP2 or DFT.[11]

At first sight, B3LYP appears to be indeed more reliable than the SCS-MP2 model (Table 1 and 2). However, both procedures might just mark the boundaries of a high-fidelity zone, the truth lying somewhere in the middle. According to the results with the B3LYP method, chlorobenzene (see Table 2, above) is more acidic than fluorobenzene by

Table 1. Deprotonation enthalpies [in kcal mol^{-1}] of benzene and its mono-, di-, tri-, tetra-, and pentafluoro-substituted congeners at various ab initio levels in the framework of the MP2 theory or the B3LYP density functional and, where applicable, in comparison with experimental[4] gas-phase data.

Benzenide	MP2// RHF[a]	B3LYP// B3LYP[b]	MP2// B3LYP[c]	MP2// B3LYP[d]	SCS// B3LYP[e]	B3LYP// B3LYP[f]	Exptl.
unsubstituted	399.0	405.4	403.9	397.6	400.2	400.1	401.7
2-F	385.9	392.9	391.5	384.9	387.9	387.4	387.2
3-F	389.6	398.8	397.9	391.7	394.0	393.6	–
4-F	391.1	401.0	399.5	393.2	395.7	395.8	–
2,3-F_2	375.6	385.9	385.3	378.6	381.5	380.3	378.1
2,4-F_2	377.2	388.5	387.0	380.5	383.4	383.1	–
2,5-F_2	375.9	386.7	385.9	379.3	382.0	381.3	380.5
2,6-F_2	370.6	380.3	378.9	371.8	375.2	374.5	374.0
3,4-F_2	382.7	395.2	394.2	388.0	390.3	390.1	–
3,5-F_2	380.3	392.4	392.1	385.9	388.1	387.3	–
2,3,4-F_3	368.7	382.0	381.4	374.7	377.5	376.6	375.7
2,3,5-F_3	366.5	379.6	379.6	372.9	375.6	374.1	–
2,3,6-F_3	361.7	373.8	373.1	366.0	369.3	368.1	370.4
2,4,5-F_3	368.9	382.8	381.9	375.3	378.0	377.4	–
2,4,6-F_3	363.0	376.0	374.5	367.6	370.9	370.3	370.0
3,4,5-F_3	374.1	388.8	388.5	382.3	384.4	383.7	–
2,3,4,5-F_4	360.0	375.7	375.7	369.0	371.6	370.2	370.0
2,3,4,6-F_4	354.6	369.6	368.8	361.8	365.0	363.9	363.5
2,3,5,6-F_4	352.5	366.8	366.8	359.7	362.9	361.1	361.6
F_5	345.6	362.6	362.5	355.3	358.5	356.7	356.8
error[g]	6.5	5.7	4.9	2.0	1.5	0.8	–

[a] MP2/6–311+G*//RHF/6–311+G*. [b] B3LYP/cc-pVTZ//B3LYP/cc-pVTZ. [c] MP2/cc-pVTZ//B3LYP/cc-pVTZ. [d] MP2/aug-cc-pVTZ//B3LYP/cc-pVTZ. [e] SCS-MP2/aug-cc-pVTZ//B3LYP/cc-pVTZ. [f] B3LYP/aug-cc-p-VTZ//B3LYP/cc-pVTZ. [g] Mean absolute error between calculated and experimental deprotonation enthalpies.

Table 2. Deprotonation enthalpies [in kcal mol^{-1}] of benzene and its mono-, di-, tri-, tetra- and pentachloro substituted congeners at various ab initio levels in the framework of the MP2 theory or the B3LYP density functional and, where applicable, in comparison with experimental[5] gas-phase data.

Benzenide	MP2// RHF[a]	MP2// B3LYP[b]	SCS// B3LYP[c]	B3LYP// B3LYP[d]	Exptl.
unsubsituted	399.0	397.6	400.2	400.1	401.7
2-Cl	385.2	385.6	388.4	385.6	386.6
3-Cl	387.1	389.0	391.6	390.3	–
4-Cl	389.7	390.4	392.9	392.5	–
2,3-Cl_2	376.3	379.1	382.0	378.4	377.1
2,4-Cl_2	377.0	379.0	381.8	379.1	–
2,5-Cl_2	374.6	377.5	380.3	377.2	377.0
2,6-Cl_2	371.9	373.5	376.7	372.3	374.0
3,4-Cl_2	380.9	383.8	386.2	385.2	–
3,5-Cl_2	376.1	380.8	383.4	380.7	–
2,3,4-Cl_3	370.9	374.5	377.2	374.1	374.9
2,3,5-Cl_3	366.3	371.1	374.0	370.1	–
2,3,6-Cl_3	364.2	367.3	370.5	366.1	370.3
2,4,5-Cl_3	369.0	372.5	375.1	372.5	–
2,4,6-Cl_3	364.7	367.7	370.8	366.7	369.2
3,4,5-Cl_3	372.4	377.4	379.7	378.0	–
2,3,4,5-Cl_4	362.9	368.1	370.8	367.2	368.3
2,3,4,6-Cl_4	359.2	363.7	366.7	362.2	363.3
2,3,5,6-Cl_4	356.5	361.7	364.9	359.9	361.8
Cl_5	353.4	359.2	362.3	357.1	355.0
error[e]	3.4	1.5	2.9	1.6	–

[a] MP2/6–311+G*//RHF/6–311+G*. [b] MP2/aug-cc-pVTZ//B3LYP/cc-pVTZ. [c] SCS-MP2/aug-cc-pVTZ//B3LYP/cc-pVTZ. [d] B3LYP/aug-cc-p-VTZ//B3LYP/cc-pVTZ. [e] Mean absolute error between calculated and experimental deprotonation enthalpies.

1.8 kcal mol^{-1} but the opposite is true according to the results obtained with the SCS-MP2 method, for which the acidity of fluorobenzene tops that of chlorobenzene by 0.5 kcal mol^{-1}. Experimentally hardly any difference is found, chlorobenzene having been assessed more acidic by merely 0.2[12] or 0.6 kcal mol^{-1}.[4,5]

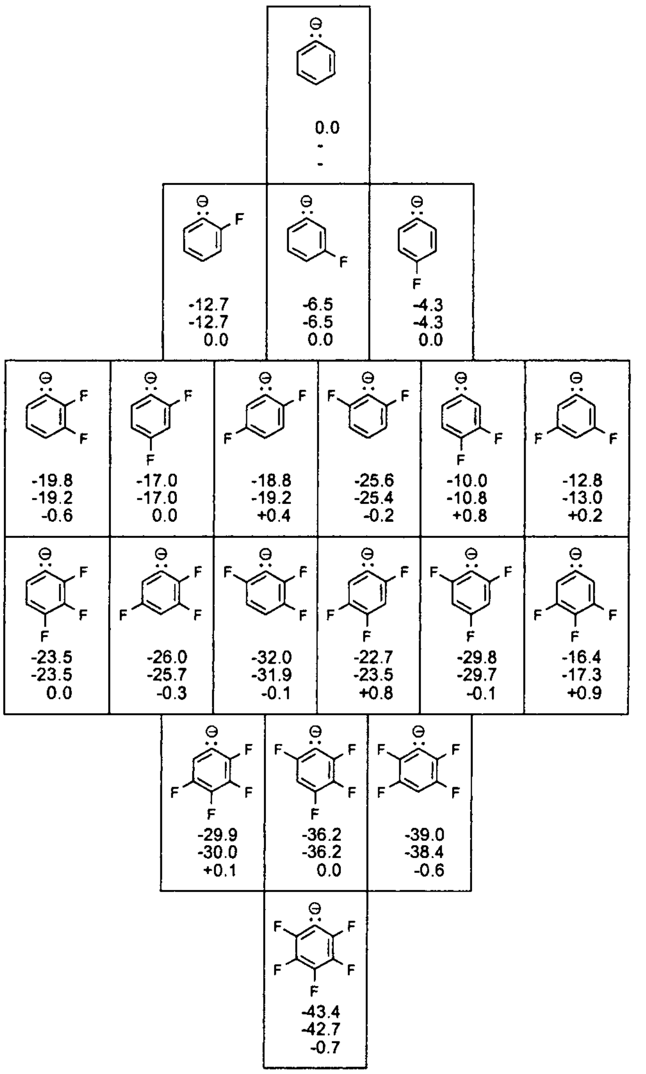
Discussion

The desired degree of accuracy achieved, we found ourselves in a position to settle the additivity/non-additivity issue definitively. In particular, we intended to scrutinize the validity of the Maksić approach[13] in this context. This formalism extracts atom- or group-specific increments from a comparison of the computed proton affinities of *ortho*-, *meta*-, and *para*-substituted phenyl anions with that of the parent benzenide itself. The next step is to use this set of increments to predict the proton affinities of doubly substituted phenyl ions and to contrast the results with the values obtained by direct quantum-chemical calculation. A close numerical agreement is taken as evidence for the additivity of the substituent effects under inspection.[13]

If we apply these criteria, we have to rule that both halogens, fluorine as well as chlorine, exhibit additivity of their substituent effects. The increment-derived protonation enthalpies deviate from the directly computed ones by 0.4 kcal mol^{-1} in the fluoro series and by 1.5 kcal mol^{-1} in the chloro series. The already excellent approximation encountered with the ensemble of dichlorophenyl anions can still be reduced to 1.0 kcal mol^{-1} if one eliminates those species having the substituent in the critical vicinal positions (see below).

However, diagnostically significant differences between increment-based and directly computed protonation enthalpies manifest themselves only at higher levels of substitution. As the difference remains below 1.0 kcal mol^{-1} in the entire fluoro series (Table 3), it was well justified to call fluorine effects additive.[4] In contrast and as suspected previously,[5] the effects exerted by chlorine are progressively attenuated when the number of substituents increases. Where-

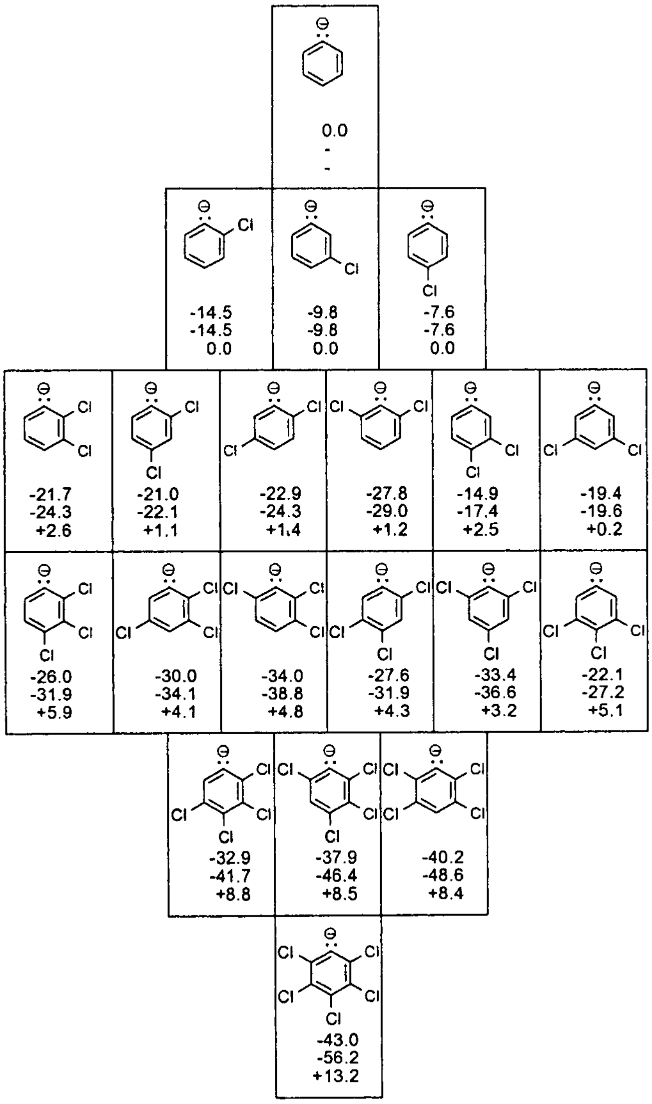
Table 3. Proton affinities[a] of zero-, mono-, di-, tetra- and pentafluoro substituted benzenides (phenyl anions) relative to the benzenide parent ion ($\Delta\Delta H^{\circ}_{g}=0.0$; $\Delta H^{\circ}_{g}=400.1$ kcal mol^{-1}): directly computed numbers[b] (upper row), increment derived numbers[c] (middle row) and differences between the two numbers (bottom row).



[a] All numbers in kcal mol^{-1}. [b] B3LYP/aug-cc-pVTZ//B3LYP/cc-pVTZ. [c] Each fluorine atom in *ortho*, *meta*, and *para* to the carbanion center is assumed to lower the proton affinity by 12.7, 6.5, and 4.3 kcal mol^{-1}, respectively.

as the differences between increment-derived and directly computed basicities are inconspicuously small at the dichlorobenzenide stage (1.5 kcal mol^{-1}; see above), they soar to 4.6 kcal mol^{-1} at the trichlorobenzenide level and explode to 8.6 and 13.2 kcal mol^{-1} with tetra- and pentachlorobenzenides, respectively (Table 4).

Table 4. Proton affinities[a] of zero-, mono-, di-, tetra-, and pentachloro-substituted benzenides (phenyl anions) relative to the benzenide parent ion ($\Delta\Delta H^{\circ}_{g}=0.0$; $\Delta H^{\circ}_{g}=400.1$ kcal mol^{-1}): directly computed numbers[b] (upper row), increment derived numbers[c] (middle row) and differences between the two numbers (bottom row).



[a] All numbers in kcal mol^{-1}. [b] B3LYP/aug-cc-pVTZ//B3LYP/cc-pVTZ. [c] Each fluorine atom in *ortho*, *meta*, and *para* to the carbanion center is assumed to lower the proton affinity by 14.5, 9.8, and 7.6 kcal mol^{-1}, respectively.

The most intriguing challenge is of course to find out what makes fluorine and chlorine substituents behave so differently. We will initially put forward a few tentative ideas. The most crucial dissimilarity between the two halogens are obviously the bond lengths. Small substituents such as fluorine will restrict the aromatic π-cloud to its ordinary confinements. The electronegative substituent will thus mainly act on the σ-skeleton. Although we fully share O. Exner's warning[14] about the "through-bond" and "through-space" vocabulary, we admit to visualize the acidity-enhancement caused by fluorine atoms as an inductive, σ-bond-polarizing effect. This effect should be linearly cumulative when two or several substituents are present. In contrast, aromatic π-electron density can flow above and below the long, hence "electronically diluted" carbon–chlorine bonds toward the halogen. This expansion of the π-cloud (the spilling over the hexagon boundaries) will increase in absolute terms with each additional substituent but will get proportionally more and more attenuated as the carbanionic center gets progressively depleted of π electrons due to σ/π-coupling.[15–19]

The (formerly) so-called d-orbital resonance,[16] a special case of π- (or n-)polarization, also shows this trend, if weakly. The progressive replacement of the first, second, and third hydrogen by chlorine atoms diminishes the gas-phase basicity of the methyl anion (methanide) by 21, 20, and 19 kcal mol^{-1}.[17–23]

As briefly mentioned above, the increment-based proton affinities of the 2,3- and 3,4-dichlorophenyl anion deviate more markedly (by 2.6 and 2.5 kcal mol^{-1}) from the directly calculated numbers than this is the case with the other four dichlorobenzenides (average difference of 1.0 kcal mol^{-1}). This suggests a special interaction between the vicinal chlorine atoms. Such an effect is well compatible with our hypothesis of an expansion of electron density from the center of the arene to the peripheral substituents. Owing to σ/π-coupling,[15–19] the polarity in the CCl axis and, as a corollary, the CCl dipole moment will be enhanced. This polarization is impeded from developing fully in the case when two neighboring chlorine atoms impose a quasi-parallel alignment of two adjacent dipoles.

As matters stand at present, it may be premature to think of generalizations. However, if the bond length to the substituent is the decisive factor as suggested above, we would not be surprised to find additivity of individual substituent effects on the acidity of arenes with all first-row elements (such as fluorine, oxygen, and saturated carbon), but non-additivity with all second and higher row elements (such as chlorine, bromine, and sulfur).

Experimental Section

The deprotonation energies of all oligofluorobenzenes, the key result of a previous gas-phase study, have already been reported in a short communication.[4] Because of their importance in the given context, we specify below what instrument was used and how the measurements were performed. For further experimental details and formalities, see previous articles from these laboratories.[5,7,24–26]

Gas-phase acidity measurements: The experiments were performed in a home-made Fourier transform ion cyclotron resonance (FT-ICR) mass

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spectrometer, equipped with a 1.4 T electromagnet and a cubic inch cell. Details of the instrument, the experimental procedures, and the error estimation have been described previously.[5,7,24–26]

The proton transfer from $H{-}A_{(F)_n}$ to $A^{\ominus}_{ref}$ and from $H{-}A_{ref}$ to $A^{\ominus}_{A_{(F)_n}}$ was studied by monitoring the reactions of the mass-selected anions as a function of the reaction time until the equilibrium was achieved, in general 3 to 4 s. Relative acidities [kcal mol^{-1}] were calculated as $\Delta\Delta G^{o}_{g} = -RT(\ln K)$, where R is the gas constant, T the absolute temperature, and K the proton-transfer equilibrium constant ($K = [A^{\ominus}_{A_{(F)_n}}][H{-}A_{ref}]/[A^{\ominus}_{ref}][H{-}A_{(F)_n}]$. The required equilibrium ion-abundance ratios ($[A^{\ominus}_{A_{(F)_n}}]/[A^{\ominus}_{ref}]$) were taken directly from the peak intensities in the reaction mixture.

The ratios of the concentration of the neutrals ($[H{-}A_{ref}]/[H{-}A_{(F)_n}]$) are equal to the partial pressure ratios, which were calculated from the partial pressures read by the ionization-gauge manometer and corrected for the ion-gauge sensitivities R^x relative to N_2 ($R^x = 1.00$). For all reference acids employed, with the exception of fluorobenzene and *m*- and *p*-fluoroaniline, experimental values for R^x are available from the literature.[27] The relative sensitivities R^x of all other acids followed from the relationship $R^x = 0.36\alpha + 0.3$.[27] The polarizabilities α were calculated[28] if experimental values[28] were unavailable.

The relative free energies ($\Delta\Delta G^{o}_{g}$) measured were converted into the free energies of gas-phase deprotonation (ΔG^{o}_{g}, listed in Table 5) by correlating them with the established free deprotonation energies of the reference acids employed (Table 5). The deprotonation enthalpies ΔH^{o}_{g} (Table 5) were calculated in the usual way[6] by adding to the free energies ΔG^{o}_{g} a term $T \times \Delta S^{o}_{g}$ which comprises the effect of the entropy change due to proton detachment (7.7 kcal mol^{-1}) and due to the change in rotational symmetry (calculated as the logarithmic ratio of the symmetry numbers of external rotations of $H{-}A_{(F)_n}$ and $A^{\ominus}_{A_{(F)_n}}$ multiplied by RT).

Table 5. Acid/base equilibrations performed between oligofluorobenzene and reference compounds in the gas phase : deprotonation energies (ΔG^{o}_{g}) and enthalpies (ΔH^{o}_{g}) [in kcal mol^{-1}].

Benzene $[H{-}A_{(F)_n}]$	Reference acid $[H{-}A_{ref}]$[a]	ΔG^{o}_{g}	ΔH^{o}_{g}
parent cmpd	–	392.9[b]	401.7[b]
F_1	-	378.8[c]	387.2[c]
1,2-F_2	-	369.7	378.1
1,3-F_2	acetonitrile (365.0)	366.4[d]	374.0[d]
1,4-F_2	methanol (380.5)	372.4[e]	380.5[e]
1,2,3-F_3	propionitrile (367.4)	367.6	375.7
1,2,4-F_3	2-butanone (361.4)	362.8	370.4
1,3,5-F_3	2-butanone (361.4)	361.6	370.0
1,2,3,4-F_4	2-butanone (361.4)	361.9	370.0
1,2,3,5-F_4	2-fluoroaniline (355.4)	355.6	363.5
1,2,4,5-F_4	3-fluoroaniline (354.0)	353.5	361.6
F_5	nitromethane (349.7)	349.2	356.8

[a] In parentheses gas-phase deprotonation data taken from reference [23]. [b] Reference [29]. [c] Reference [12]. [d] Virtually the same numbers are obtained when proprionitrile (367.4[23]) is employed as the reference acid. [e] Reference [30].

Computational work: Initially the geometries of all 19 fluorinated phenyl anions and the corresponding *CH*-acids were optimized with the RHF method by using the 6–311G basis set supplemented with polarization functions of d-type symmetry[31] at the carbanionic center and at each of the two neighboring carbon centers. To better describe the electron density distribution of the carbanionic lone pair a diffuse sp-orbital[32,33] was included at the carbanionic center. This RHF/6–311+G* method was also used for the calculation of the zero-point vibrational energies (ZPVEs). All optimized structures adopted planar arrangements (C_s) and were located as minima on their potential energy surfaces. The deprotonation energies were calculated at the second-order Møller–Plesset perturbation theory level.[34] The electronic energies were converted to enthalpies at 298 K, where the ZPVEs were multiplied by the scale factor of 0.89.[35] These MP2/6–311+G*//RHF/6–311+G* calculations were carried out with the GAMESS program.[36]

To establish how the numerical outcome depends on the quantum-chemical method and basis set employed we continued with geometry optimization at the B3LYP[10] level using the correlation consistent cc-pVTZ basis set[37] and we have performed single-point calculations with the MP2, and SCS-MP2 methods.[34,11] To evaluate the significance of diffuse functions on all atoms we tested next the aug-cc-pVTZ basis set.[37] The B3LYP, MP2, and SCS-MP2 calculations with the cc-pVTZ and aug-cc-pVTZ basis sets were carried out with the TURBOMOLE package of programs.[38] In these MP2 treatments the resolution of the identity technique (RIMP2)[39] was applied and the correlation of the 1s electrons of carbon and fluorine and the 1s, 2s, and 2p electrons of chlorine was excluded (frozen core approximation). The corresponding auxiliary basis sets for the RIMP2 calculations were taken from the TURBOMOLE basis set library.[38,40,41] According to prior experience, the errors due to the RI approximation are less than 0.01 kcal mol^{-1} for energy differences as considered here. To calculate the corresponding B3LYP, MP2, and SCS-MP2 deprotonation enthalpies we have used ZPVEs and thermal corrections from harmonic vibrational analyses carried out at the B3LYP/cc-pVTZ level with the SNF program.[42]

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[1] F. Mongin, R. Maggi, M. Schlosser, *Chimia* **1996**, *50*, 650–652.

[2] M. Schlosser, *Eur. J. Org. Chem.* **2001**, 3975–3984.

[3] M. Schlosser in *Organometallics in Synthesis : A Manual* (Ed.: M. Schlosser), 2nd ed, Wiley, Chichester, **2002**, pp. 1–352, spec. 185–284.

[4] H. H. Büker, N. M. M. Nibbering, D. Espinosa, F. Mongin, M. Schlosser, *Tetrahedron Lett.* **1997**, *38*, 8519–8522.

[5] M. Schlosser, E. Marzi, F. Cottet, H. H. Büker, N. M. M. Nibbering, *Chem. Eur. J.* **2001**, *7*, 3511–3516.

[6] J. E. Bartmess, R. T. McIver in *Gas Phase Ion Chemistry*, Vol. *2* (Ed.: M. Bowers), Academic Press, New York, **1979**, pp. 87–121, spec. 94–97.

[7] M. Schlosser, F. Mongin, J. Porwisiak, W. Dmowski, H. H. Büker, N. M. M. Nibbering, *Chem. Eur. J.* **1998**, *4*, 1281–1286.

[8] P. G. Wenthold, R. R. Squires, *J. Mass Spectrom.* **1995**, *30*, 17–24 [Chem. Abstr. **1995**, *122*, 186864a].

[9] C. H. DePuy, S. Gronert, S. E. Barlow, V. M. Bierbaum, R. Damrauer, *J. Am. Chem. Soc.* **1989**, *111*, 1968–1973.

[10] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200–1211; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[11] a) S. Grimme, *J. Chem. Phys.* **2003**, *118*, 9095–9102; b) S. Grimme, *J. Comput. Chem.* **2003**, *24*, 1529–1537; c) M. Piacenza, S. Grimme, *J. Comput. Chem.* **2004**, *25*, 83–98; d) S. Grimme, M. Gerenkamp, *Chem. Phys. Lett.* **2004**, *392*, 229 –235; e) S. Grimme, *Chem. Eur. J.* **2004**, *10*, 3423–3429; f) I. Hyla-Kryspin, S. Grimme, *Organometallics* **2004**, *23*, 5581–5592.

[12] P. B. M. Andrade, J. M. Riveros, *J. Mass Spectrom.* **1996**, *31*, 767–770 [Chem. Abstr. **1996**, *125*, 247111p].

[13] Z. B. Maksić, D. Kovaček, M. Eckert-Maksić, I. Zrinski, *J. Org. Chem.* **1996**, *61*, 6717–6719.

[14] O. Exner, S. Böhm, *Chem. Eur. J.* **2003**, *9*, 4718–4723.

[15] M. Schlosser, R. Lehmann, T. Jenny, *J. Organomet. Chem.* **1990**, *389*, 149–157.

[16] M. Schlosser, J. H. Choi, S. Takagishi, *Tetrahedron* **1990**, *46*, 5633–5648.

[17] Z.-p. Liu, M. Schlosser, *Heteroat. Chem.* **1991**, *2*, 515–519 [Chem. Abstr. **1992**, *116*, 83693y].

[18] E. Baston, R. Maggi, K. Friedrich, M. Schlosser, *Eur. J. Org. Chem.* **2001**, 3985–3989.

[19] E. Castagnetti, M. Schlosser, *Chem. Eur. J.* **2002**, *8*, 799–804.

[20] W. V. E. Doering, A.K. Hoffmann, *J. Am. Chem. Soc.* **1955**, *77*, 521–526.

[21] B. Römer, G. G. Gatev, M. Zhong, J. I. Brauman, *J. Am. Chem. Soc.* **1998**, *120*, 2919–2924.

[22] K. M. Ervin, W. C. Lineberger, *J. Phys. Chem.* **1991**, *95*, 1167–1177.

[23] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, "Ion Energetics Data", in *NIST Chemistry WebBook : NIST Standard Reference Data Base Number 69* (Eds. : P. J. Linstrom, W. G. Mallard), update July 2001, Nat. Institute of Standards and Technol., Gaithersburg, MD (http://webbook.nist.gov).

[24] M. Born, S. Ingemann, N. M. M. Nibbering, *Int. J. Mass Spectrom.* **2000**, *194*, 103–113 [Chem. Abstr. **2000**, *132*, 165918].

[25] L. J. de Konig, C. W. F. Kort, F. A. Pinkse, N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Processes*, **1989**, *95*, 71–92 [Chem. Abstr. **1990**, *112*, 171115b].

[26] R. A. L. Peerboom, S. Ingemann, N. M. M. Nibbering, J. F. Liebman, *J. Chem. Soc. Perkin Trans. 2* **1990**, 1825–1828.

[27] J. E. Bartmess, R. M. Georgiadis, *Vacuum* **1983**, *33*, 149–153 [Chem. Abstr. **1983**, *99*, 7263r].

[28] K. J. Miller, J.A. Savchik, *J. Am. Chem. Soc.* **1990**, *112*, 7206–7213.

[29] G. E. Davico, V. M. Bierbaum, C. H. DePuy, G. B. Ellison, R. R. Squires, *J. Am. Chem. Soc.* **1995**, *117*, 2590–2599.

[30] H. E. K. Matimba, S. Ingemann, N. M. M. Nibbering, *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 73–81 [Chem. Abstr. **1993**, *118*, 254313q].

[31] W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. DeFrees, J.A. Pople, J. S. Binkley, *J. Am. Chem. Soc.* **1982**, *104*, 5039–5048.

[32] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. von R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294–301 [Chem. Abstr. **1983**, *99*, 128531k].

[33] M. J. Frisch, J.A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265–3269.

[34] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618–622.

[35] W. J. Hehre, L. Radom, P. von R. Schleyer, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**.

[36] M. W. Schmidt, K.K. Baldridge, J.A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, M. Matsunaga, K.A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J.A. Montgomery, *J. Comput. Chem.* **1993**, *14*, 1347–1363 [Chem. Abstr. **1994**, *120*, 15297x].

[37] a) T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007–1023; b) R. A. Kendall, T. H. Dunning, R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796–6806. c) D. E. Woon, T. H. Dunning, *J. Chem. Phys.* **1993**, *98*, 1358–1371; d) D. E. Woon, T. H. Dunning, *J. Chem. Phys.* **1994**, *100*, 2975–2988.

[38] R. Ahlrichs, M. Bär, H.-P. Baron, R. Bauernschmitt, S. Böcker, M. Ehrig, K. Eichkorn, F. Elliot, F. Furche, F. Haase, M. Häser, H. Horn, C. Huber, H. Huniar, M. Kattanek, C. Kölmel, M. Kollowitz, K. May, C. Ochsenfeld, H. Öhm, A. Schäfer, U. Schneider, O. Treutler, M. von Arnim, F. Weigend, P. Weis, H. Weiss, TURBOMOLE (Vers. 5.5) University, Karlsruhe, **2002**.

[39] O. Vahtras, J. Almlöf, M. W. Feyereisen, *Chem. Phys. Lett.* **1993**, *213*, 514–518.

[40] The basis set is available from the TURBOMOLE homepage (http://www.turbomole.com) by using the FTP Server Button in the subdirectory cbasen.

[41] F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143–152.

[42] O. Kind, M. Reiher, J. Neugebauer, B. A. Hess, SNF (Vers. 2.2.1), Program Package for Numerical Frequency Analyses, University, Erlangen (Germany), **2002**.

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