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Gas-phase acidity, bond dissociation energy and enthalpy of formation of fluorine-substituted benzenes: A theoretical study

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ABSTRACT

A variety of theoretical methods have been used to study the gas-phase acidity of benzene and its eleven fluorine-substituted derivatives: fluorobenzene, three isomers of difluorobenezene, three isomers of trifluorobenzene, three isomers of tetrafluorobenzene and 1,2,3,4,5-pentafluorobenzene. The high-level ab initio methods, G3//B3-LYP and CBS-QB3, are shown to reproduce experimental data to within an average of 1.9 and 1.4 kcal mol^{-1}, respectively. Of the lower-cost methods studied, M05-2X and MP2 showed the best overall performance with mean absolute deviations of just 1.2 and 1.1 kcal mol^{-1}, respectively. The effect of substitution and position on the acidity of the protons in the various compounds are studied and the structure–reactivity trends in these heterolytic C–H bond dissociation energies (BDEs) are compared with the corresponding homolytic C–H BDEs for the same species.

1. Introduction

Fluorine as a substituent has a unique effect on chemical properties owing to its high electronegativity. It has been well documented that fluorine substituents significantly increase the acidity of benzene. For example, Büker et al. [1] showed that the gas-phase deprotonation of fluorobenzene is 12.3 kcal mol^{-1} more than benzene, but 12.3 kcal mol^{-1} less than 1,3-difluorobenzene; the acidity of 1,3,5-trifluorobenzene is 4.9 kcal mol^{-1} more than 1,3-difluorobenzene, but 4.0 kcal mol^{-1} less than 1,2,3,5-tetrafluorobenzene; the acidity of pentafluorobenzene is almost 42 kcal mol^{-1} more than benzene, an increase of more than 10% of the total deprotonation free energy. The positions of fluorine atoms are also important; thus, 1,2-difluorobenzene and 1,4-difluorobenzene are much less acidic than 1,3-difluorobenzene [1].

The deprotonation of fluorobenzenes is an efficacious means to generate reactive intermediates that can be used to incorporate halogen-bearing building blocks into substances of potential use as pharmaceuticals or agrochemicals. Studies on protonation or deprotonation are thus of practical importance since these processes are often required to initiate chemical reactions [1]. In continuation of our previous study on fluorinated compounds [2,3], we have been attracted to study fluorobenzenes in order to assess the ability of recently developed computational methods for the calculation of acidity of fluorinated compounds. Modeling of fluorine-substituted compounds can sometimes be problematic [4], and it is of interest to determine whether the same level of accuracy can be achieved for compounds with fluorine atoms.

In the present work, we report the results of high-level ab initio calculations of the gas-phase deprotonation of fluorobenzenes. We first examine the accuracy of high-level ab initio methods through comparison with experiment. We then use our computational methods to study the effect of substitution and position on the acidity of the protons in the various compounds. We also compare the structure–reactivity trends in these heterolytic C–H bond dissociation energies (BDEs) with the corresponding homolytic C–H BDEs for the same species. These latter quantities are important as hydrogen atom abstraction is a key step in the atmospheric degradation of hydrofluorocarbons (HFCs) [5].

2. Computational methods

Standard ab initio molecular orbital theory [6] and density functional theory (DFT) [7] calculations were performed using Gaussian 03 [8]. Geometries of all species were optimized using various levels of theory, and where necessary, extra care was taken to select the correct symmetrical point group of each species. The

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nature of each stationary point was established via frequency calculations. The optimized geometries were then used for higher-level single-point energy calculations at various levels of theory, as described below. Using these data, the enthalpies, entropies and free energies of each species were then calculated via the standard textbook formulae for an ideal gas under harmonic oscillator and rigid rotor approximations. For the gas-phase enthalpy and Gibbs free energy of proton, we have used the literature values of 1.48 kcal mol^{-1} and −6.28 kcal mol^{-1}, respectively [9–11]. Enthalpies of formation were calculated using the methodology described by Nicolaides et al. [12], as detailed in our previous study [11]. Further details are provided in the Supporting Information.

Our benchmark levels of theory in the present work are G3//B3-LYP [13] and CBS-QB3 [14]. These composite methods approximate CCSD(T) or QCISD(T) calculations with a large triple zeta basis set via addivity and/or extrapolation procedures at the MP2 and/or MP4 levels of theory, and have been demonstrated to provide "chemical accuracy" (ca. 1.0 kcal mol^{-1}) when assessed against large test sets of thermochemical data [13,14]. Full descriptions of these methods can be found in their original references [13,14]. Calculations were also performed using a variety of lower levels of theory in order to establish whether these lower-cost procedures could deliver acceptable accuracy for the present systems. Among the methods examined were a selection of DFT functionals, including a typical pure generalized gradient approximation functional, PBEPBE [15], the widely used hybrid functional, B3-LYP [16], a newer hybrid functional, MPWB1K [17], and two of the new generation functionals that include terms based on the kinetic energy density, BMK [18], and M05-2X [19]. We also included the ab initio method, MP2, which has performed well in our studies of other chemical reactions [20]. These single-point energy calculations were carried out in conjunction with the 6-311 + G(3df, 2p) basis set using B3-LYP/6-31G(d) optimized geometries.

The G3//B3-LYP method employs the geometry optimizations (and frequency calculations) at the B3-LYP/6-31G(d) level; CBS-QB3 employs B3-LYP/CBSB7 (B3-LYP/6-311G(2d, d, p)) [13,14]. In the present work we have used these proscribed levels of theory when applying the respective composite procedures. However, we were also interested in whether their accuracy is affected by the use of B3-LYP geometries. To this end, we also conducted a small assessment study in which geometries were optimized at a variety

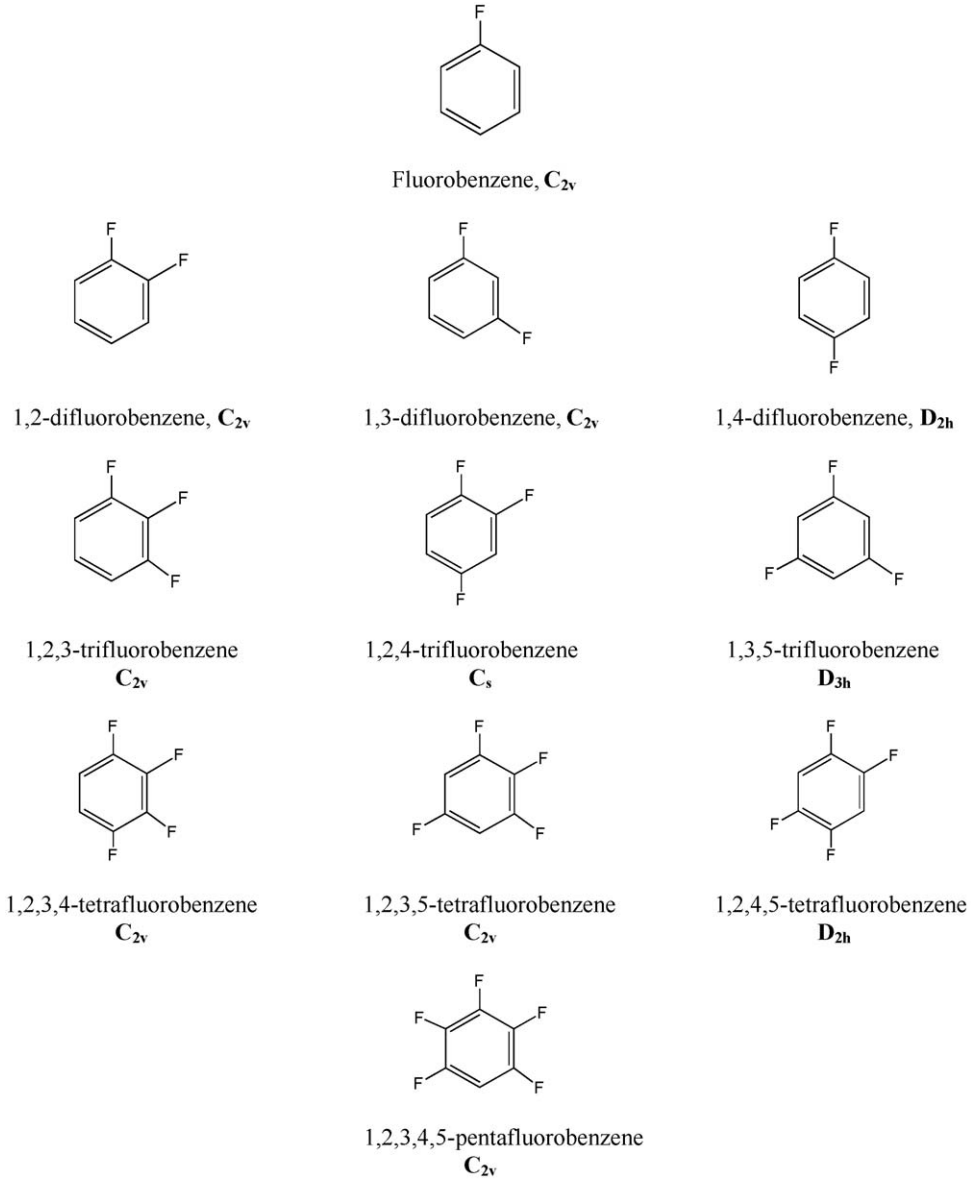


Fig. 1. Studied fluorobenzenes with their point group.

Table 1
Comparison of calculated and experimental [1] values of the enthalpy (ΔH) and Gibbs free energy (ΔG) of deprotonation for benzene and its fluorene-substituted derivatives (298 K, kcal mol^{-1}).

Species	ΔH			ΔG		
	G3B3[a]	CBS-QB3	Exp.	G3B3[a]	CBS-QB3	Exp.
Benzene	400.8	400.5	400.7	392.0	391.6	390.9
Fluorobenzene	388.6	387.9	386.9	380.3	379.7	378.6
1,2-Difluorobenzene	381.9	381.8	377.9	373.6	373.4	369.5
1,4-Difluorobenzene	382.4	382.2	380.2	373.7	373.5	372.1
1,3-Difluorobenzene	376.0	375.0	373.9	368.2	367.1	366.3
1,2,3-Trifluorobenzene	378.1	377.5	375.5	369.8	369.2	367.3
1,2,4-Trifluorobenzene	369.7	369.1	370.2	361.8	361.2	362.6
1,3,5-Trifluorobenzene	371.7	371.1	369.7	363.2	362.6	361.4
1,2,3,4-Tetrafluorobenzene	371.9	371.7	369.7	363.5	363.3	361.6
1,2,3,5-Tetrafluorobenzene	365.6	364.5	363.3	357.3	356.2	355.4
1,2,4,5-Tetrafluorobenzene	362.9	362.7	361.4	354.6	354.4	353.3
1,2,3,4,5-Pentafluorobenzene	358.6	357.9	356.6	350.7	350.0	349.0
Mean Absolute Deviation	1.9	1.5		1.9	1.4	

[a] G3B3 stands for G3//B3-LYP.

of levels of theory (HF, B3-LYP, MP2 and QCISD). To evaluate the effect of the geometry optimization on the calculated reaction energy, single-point energies were then calculated on the various optimized geometries at a consistent level of theory, QCISD/6–311 + G(d, p).

3. Results and discussion

3.1. Assessment of theoretical procedures

In this work, we have studied benzene and its eleven fluorine-substituted compounds: fluorobenzene, three difluorobenezenes (1,2-difluorobenezene, 1,3-difluorobenezene, and 1,4-difluorobenezene), three trifluorobenzenes (1,2,3-trifluorobenzene, 1,2,4-trifluorobenzene, 1,3,5-trifluorobenzene), three tetrafluorobenzenes (1,2,3,4-tetrafluorobenzene, 1,2,3,5-tetrafluorobenzene, 1,2,4,5-tetrafluorobenzene) and 1,2,3,4,5-pentafluorobenzene (see Fig. 1 for structures). The deprotonation of all these compounds have been studied experimentally by Büker et al. [1]. They measured the ion concentrations of these species using ion cyclotron resonance (ICR) mass spectrometry and reported Gibbs energy change of deprotonation of the studied species. They also calculated the enthalpy change of deprotonation reaction from Gibbs energy changes by taking into account the entropy changes due to proton dissociation and rotational symmetry changes [1].

Table 1 presents the calculated changes of enthalpy and Gibbs free energy (gas-phase acidity) for the deprotonation of the studied species using our benchmark levels of theory, along with the corresponding experimental values. Both levels of theory provide good approximations to the experimental data, having mean absolute deviations of 1.9 and 1.5 kcal mol^{-1} for G3//B3-LYP and CBS-QB3, respectively. In each case, the errors in the enthalpies and corresponding free energies are very similar, implying that the entropic calculations are not a significant additional source of error. In general, the two levels of theory studied tend to overestimate the gas-phase acidities of the fluorobenzenes, and these errors tend to increase slightly with the number of fluorine atoms on ring. For example, the deviation of G3//B3-LYP from experiment for benzene is 0.1 kcal mol^{-1}, for fluorobenzene it is 1.7 kcal mol^{-1}, for 1,4-difluorobenzene it is 2.2 kcal mol^{-1} and for 1,2,3-trifluorobenzene it is 2.6 kcal mol^{-1}. However, there is an additional extraordinary discrepancy for 1,2-difluorobenzene. In this case the deviation is 4.0 kcal mol^{-1} at G3//B3-LYP (3.9 kcal mol^{-1} for CBS-QB3), which may indicate additional error in the experimental value for this system.

Since different basis sets are used for the geometry optimization in G3//B3-LYP and CBS-QB3 methods, we conducted a small assessment study to establish whether these differences affected the accuracy of the results. To this end, we optimized the geometries of three species: benzene, fluorobenzene and 1,2-difluorobenzene and their anions using a variety of different methods (B3-LYP, HF, MP2 and QCISD with various basis sets), and then calculated single-point energies on each of the optimized geometries at a consistent level of theory, QCISD/6–311 + G(d, p). The resulting reaction enthalpies are provided in Table 2. From this table, it is seen that enthalpies of deprotonation are relatively

Table 2
Effect of geometry optimization of the calculated enthalpy deprotonation for benzene and its fluorene-substituted derivatives (298 K, kcal mol^{-1}).[a].

Geometry	C_6H_6		C_6H_5F		$C_6H_4F_2$[b]	
B3-LYP/6–31G(d)	403.0	(−0.1)	390.8	(0.0)	384.0	(−0.1)
B3-LYP/6–31 + G(d)	403.0	(0.0)	390.9	(−0.1)	384.1	(−0.2)
B3-LYP/6–311 + G(d, p)	402.9	(0.0)	390.9	(−0.2)	384.2	(−0.3)
HF/6–31G(d)	402.7	(0.2)	390.6	(0.2)	383.8	(0.1)
HF/6–31 + G(d)	402.9	(0.1)	390.7	(0.1)	383.9	(0.0)
HF/6–311 + G(d, p)	402.8	(0.1)	390.6	(0.1)	383.8	(0.1)
MP2/6–31G(d)	403.1	(−0.2)	390.8	(−0.1)	384.1	(−0.2)
MP2/6–31 + G(d)	403.0	(0.0)	390.8	(0.0)	383.9	(-0.1)
MP2/6–311 + G(d, p)	403.0	(0.0)	390.8	(0.0)	384.0	(−0.1)
QCISD/6–31G(d)	403.1	(−0.1)	390.8	(−0.1)	384.0	(−0.1)
QCISD/6–31 + G(d)	402.9	(0.0)	390.7	(0.0)	383.9	(0.0)
QCISD/6–311 + G(d, p)	402.9	(0.0)	390.7	(0.0)	383.9	(0.0)

[a] The enthalpies of deprotonation are calculated from single-point energies on each of the optimized geometries at a consistent level of theory, QCISD/6–311 + G(d, p). Values in parenthesis are the deviation of each enthalpy from the benchmark level of theory (QCISD/6–311 + G(d, p)).
[b] 1,2-Difluorobenzene.

Table 3
Performance of lower-cost methods for the enthalpy of deprotonation for benzene and its fluorene-substituted derivatives (298 K, kcal mol^{-1})[a].

	B3-LYP	MPWB1K	BMK	PBEPBE	M05-2X	MP2	Exp.
Benzene	401.6	404.3	401.7	397.8	401.5	398.1	400.7
Fluorobenzene	388.9	391.9	389.4	385.1	388.3	385.6	386.9
1,2-Difluorobenzene	381.8	384.2	382.3	378.5	380.8	379.2	377.9
1,4-Difluorobenzene	382.7	385.8	383.1	379.4	381.8	380.0	380.2
1,3-Difluorobenzene	376.1	379.3	376.9	372.3	374.9	372.8	373.9
1,2,3-Trifluorobenzene	378.3	381.7	379.0	374.8	377.4	375.8	375.5
1,2,4-Trifluorobenzene	369.6	373.0	370.6	365.9	368.3	366.9	370.2
1,3,5-Trifluorobenzene	371.9	375.3	372.7	368.5	370.5	368.6	369.7
1,2,3,4-Tetrafluorobenzene	371.7	375.3	372.7	368.4	370.7	369.8	369.7
1,2,3,5-Tetrafluorobenzene	365.5	369.1	366.5	362.2	364.0	362.9	363.3
1,2,4,5-Tetrafluorobenzene	362.6	366.2	363.9	359.0	361.2	360.5	361.4
1,2,3,4,5-Pentafluorobenzene	358.1	362.0	359.6	354.5	356.7	356.1	356.6
Mean absolute deviation	2.0	5.2	2.7	1.7	1.2	1.1	

[a] All calculations performed as single points in conjunction with the 6 − 311 + G(3df, 2p) basis set using B3-LYP/6-31G(d) optimized geometries. Experimental data taken from reference [1].

unaffected by the level of theory used in the geometry optimization. It is worth noting that QCISD/6–311 + G(d, p) single-point energies based on HF geometries deviate by 1–2 kcal mol^{-1} for each species relative to QCISD/6–311 + G(d, p) geometries, but there is a systematic cancellation of error from the reaction energies and errors due to geometry optimization diminish to 0.2 kcal/mol. However, for other levels of theory (B3-LYP, MP2 and QCISD), all employed basis sets presented very small deviation even for the energy of each species compared to QCISD/6–311 + G(d, p) geometries. For more details of energy of each species see Supporting Information.

It is worth noting that, in an earlier study, Gutowski and Dixon [21] used variants of the same high-level composite procedures used in this work to study the gas- and solution-phase acidities of a series of strong Brønsted acids. They also found that these procedures were generally very accurate, with errors less than 1 kcal mol^{-1}. However, for those species having experimental acidities below 302 kcal mol^{-1} (including several fluorinated species), the errors were much larger (4–15 kcal mol^{-1}), and these were attributed to possible problems in the experimental data. Our current work, which further verifies the accuracy of these high-level theoretical procedures for fluorinated compounds, supports this earlier conclusion.

To establish whether or not lower-cost procedures are also appropriate to study the deprotonation of fluorine-substituted compounds, we also examined the performance of popular DFT methods (B3-LYP, MPWB1K, BMK, PBEPBE, M05-2X) as well as the ab initio method MP2 using 6–311 + G(3df, 2p) basis set. The B3-LYP/6–31G(d) geometries have been used for all these single-point energy calculations as in the G3//B3-LYP method (see Table 3). The lower-level methods perform remarkably well with all but MPWB1K (MAD = 5.2 kcal mol^{-1}) showing comparable performance to their higher-level counterparts. Among the lower-cost methods studied herein, the ab initio method MP2 gives the best overall performance with an MAD of 1.1 kcal mol^{-1}. The DFT method M05-2X also showed excellent performance with an average error of just 1.2 kcal mol^{-1}, and is promising as a low-cost method for the study of larger fluorinated compounds.

Finally, given the excellent performance of the studied computational methods for the calculation of enthalpy of deprotonation, it is of interest to examine the extent to which this is achieved through systematic error cancellation. To this end, we also examined the errors in the calculated heats of formation of the fluorobenzenes (Table 4). From this table, it is seen that both of the high-level composite procedures provide an excellent approximation to the available experimental data, consistent with their excellent performance for the enthalpies of deprotonation. However, as expected, at the lower levels of theory the errors in the heats of formation are generally much greater than in the deprotonation calculations. An exception to this is the method MPWB1K which gave smaller errors in the heats of formation calculation (MAD = 3.7 kcal mol^{-1}) compared with the enthalpies of deprotonation (MAD = 5.2 kcal mol^{-1}), despite the greater systematic error cancellation expected in the latter case. This presumably is related to the manner in which this method was parameterised.

3.2. Structure–reactivity trends

Using an accurate and reliable computational method it is possible to distinguish the acidity of different hydrogens in a molecule, which is a difficult task using experimental techniques. Table 5 shows the enthalpies of deprotonation for all non-equivalent hydrogens in benzene and its fluorinated derivatives. In

Table 4
Performance of computational methods for calculation of standard enthalpy of formation for benzene and some of its fluorene-substituted derivatives (298 K, kcal mol^{-1})[a].

	B3-LYP	MPWB1K	BMK	PBEPBE	M05-2X	(RO)MP2	G3B3[b]	CBS[b]	Exp.[c]
Benzene	25.2	17.2	17.6	−23.6	12.7	17.9	20.8	21.7	19.8
Fluorobenzene	−22.0	−30.4	−31.9	−80.4	−37.1	−37.8	−26.6	−26.6	−27.7
1,2-Difluorobenzene	−64.7	−73.4	−76.7	−132.7	−82.2	−88.9	−69.6	−70.9	−70.2
1,4-Difluorobenzene	−67.9	−76.6	−79.9	−135.7	−85.5	−91.9	−72.7	−73.9	−73.3
1,3-Difluorobenzene	−68.6	−77.4	−80.7	−136.5	−86.3	−92.8	−73.3	−74.2	−73.9
1,2,4,5-Tetrafluorobenzene	−151.0	−160.3	−167.0	−238.1	−173.1	−191.8	−156.3	−159.5	−154.6
1,2,3,4,5-Pentafluorobenzene	−188.4	−197.7	−206.3	−285.1	−212.3	−237.6	−193.9	−197.7	−192.8
Mean absolute deviation	5.0	3.7	7.5	65.6	13.0	21.5	1.0	2.1	

[a] All calculations except G3B3 and CBS-QB3 performed as single points in conjunction with the 6–311 + G(3df, 2p) basis set using B3-LYP/6-31G(d) optimized geometries. The deviations of the theoretical values from the experiment are shown in parentheses.
[b] G3B3 and CBS stand for G3//B3-LYP and CBS-QB3, respectively.
[c] Experimental gaseous enthalpies of formation values are taken from NIST web site [22].

Table 5
Comparison of heterolytic and homolytic C–H bond dissociation energies (ΔH 298 K, kcal mol^{-1}), calculated at the CBS-QB3 level of theory.

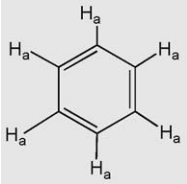
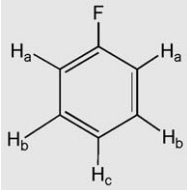
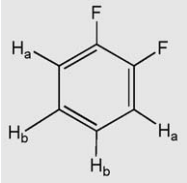
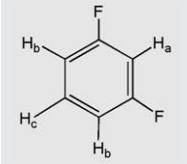
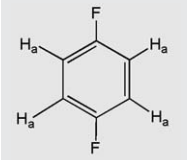
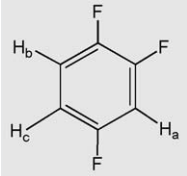
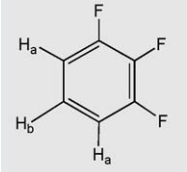
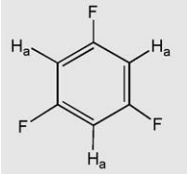
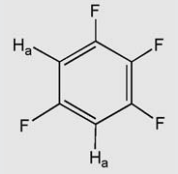
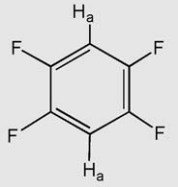
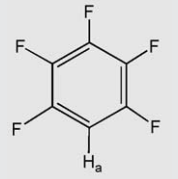
		H_a	H_b	H_c
	Heterolytic	400.5	–	–
		(0.0)	–	–
	Homolytic	115.4[a]	–	–
		(0.0)	–	–
	Heterolytic	387.9	394.2	395.8
		(0.0)	(6.3)	(7.8)
	Homolytic	118.1	115.6	116.5
		(0.0)	(−2.5)	(−1.6)
	Heterolytic	381.8	390.5	–
		(0.0)	(8.7)	–
	Homolytic	118.5	116.9	–
		(0.0)	(−1.6)	–
	Heterolytic	375.0	383.3	388.0
		(0.0)	(8.3)	(12.9)
	Homolytic	120.9	118.9	115.7
		(0.0)	(−2.0)	(−5.2)
	Heterolytic	382.2	–	–
		(0.0)	–	–
	Homolytic	118.7	–	–
		(0.0)	–	–
	Heterolytic	369.1	375.5	377.9
		(0.0)	(6.4)	(8.8)
	Homolytic	121.3	118.7	119.4
		(0.0)	(−2.6)	(−2.0)
	Heterolytic	377.5	384.5	–
		(0.0)	(7.2)	–
	Homolytic	119.1	116.8	–
		(0.0)	(−2.2)	–
	Heterolytic	371.1	–	–
		(0.0)	–	–
	Homolytic	121.4	–	–
		(0.0)	–	–

Table 5 (*Continued*)

		H_a	H_b	H_c
	Heterolytic	371.7	–	–
		(0.0)	–	–
	Homolytic	119.8	–	–
		(0.0)	–	–
	Heterolytic	364.5	–	–
		(0.0)	–	–
	Homolytic	121.8	–	–
		(0.0)	–	–
	Heterolytic	362.7	–	–
		(0.0)	–	–
	Homolytic	121.8	–	–
		(0.0)	–	–
	Heterolytic	357.9	–	–
		(0.0)	–	–
	Homolytic	122.2	–	–
		(0.0)	–	–

[a] Experimental value is 112.9 kcal mol^{-1} for benzene [23] shows a deviation of 2.5 kcal mol^{-1}. Values in parenthesis are the difference between changes of enthalpies for H_b and H_c from the corresponding values of H_a.

all cases it is clear that the acidity increases with the proximity of the acidic hydrogen to the fluorine atoms. For example, fluorobenzene has three non-equivalent hydrogens: ortho, meta and para, shown as H_a, H_b and H_c in Table 5. Using CBS-QB3 method, the change of enthalpy for the deprotonation of these hydrogens are 379.7, 385.9 and 387.9 kcal mol^{-1}, respectively. Hence, H_b and H_c are 6.3 and 8.2 kcal mol^{-1} less acidic than H_a. In a similar manner, H_b and H_c are 7.8 and 12.9 kcal mol^{-1} less acidic than H_a in 1,3-diflurobenzene, and 6.3 and 8.8 kcal mol^{-1} less acidic than H_a in 1,2,4-trifluorobenzene. There are two non-equivalent hydrogens in 1,2-difluorobenzene and 1,2,3-trifluorobenzene, and H_b is 8.7 and 7.3 kcal mol^{-1} less acidic than H_a in these derivatives, respectively. These trends are superimposed on the more general trend of the increasing acidity as the number of fluorine atoms is increased, and are due to the ability of the fluorine atoms to stabilize the resulting anion via sigma withdrawal.

The enthalpy of the deprotonation reaction can be thought of as a heterolytic C–H bond dissociation energy (BDE), reaction (1).

$$C_6H_xF_{6-x} \rightarrow C_6H_{x-1}F_{6-x}^- + H^+ \quad (1)$$

It is of interest to compare the trends in these heterolytic BDEs with those of the corresponding homolytic C–H BDEs, reaction (2).

$$C_6H_xF_{6-x} \rightarrow C_6H_{x-1}F_{6-x}^{\bullet} + H^{\bullet} \quad (2)$$

C–H BDEs for all non-equivalent C–H bonds in benzene and its fluorinated derivatives are included in Table 5. Since $C_6H_xF_{6-x}$ is common to both reactions, the differences in the two types of BDE refect the differing effects of the fluorine substituents on the stabilities of the anion and radical. These differences can also be obtained more directly as the gas-phase electron affinities of the $C_6H_{x-1}F_{6-x}^{\bullet}$ radicals (Table 6).

In contrast to the deprotonation reactions, homolytic BDEs generally *increase* with the number of fluorine atoms present and with the proximity of the breaking C–H bond to them. This is likely to be to due to the destabilizing effects of the sigma withdrawal by the fluorine atoms on the product radical, which outweighs any stabilizing effects via lone pair donation. To quantify the differing effects of fluorination on the heterolytic (ΔH_{Deprot}) and homolytic (ΔH_{BDE}) C–H BDEs of the fluorinated compounds, the respective BDEs were fitted via the following simple formulae

$$\Delta H_{Deprot.}(\text{kcal mol}^{-1}) = 400.7 - (13.1o + 6.7m + 4.9p) \quad (3)$$

$$\Delta H_{BDE}(\text{kcal mol}^{-1}) = 114.3 + (3.3o + 0.6m + 0.6p) \quad (4)$$

where: o, m and p are the integral numbers of fluorine atoms at the ortho, meta and para positions to the breaking bond.

In each case, the equation provided an excellent fit to the relevant data for benzene and all of its fluorinated derivatives (R^2 = 0.991 and 0.998 respectively, see Fig. 2). Inspection of these equations confirms that increasing fluorination in all positions leads to a decrease in the deprotonation enthalpy and an increase in the homolytic bond dissociation energy. On comparing the

Table 6
Electron affinities (kcal mol^{-1}) of studied radical species calculated at G3//B3LYP and CBS-QB3 levels of theory.

Species	Electron affinity[a]	
	G3//B3LYP	CBS-QB3
$C_6H_5^•$	28.0	28.6
$C_6H_4F^•$	43.4	43.8
1,2-$C_6H_3F_2^•$	50.5	50.4
1,4-$C_6H_3F_2^•$	50.5	50.2
1,3-$C_6H_3F_2^•$	59.2	59.6
1,2,3-$C_6H_2F_3^•$	55.4	55.3
1,2,4-$C_6H_2F_3^•$	66.1	65.9
1,3,5-$C_6H_2F_3^•$	64.6	64.0
1,2,3,4-$C_6HF_4^•$	62.4	61.8
1,2,3,5-$C_6HF_4^•$	71.1	70.9
1,2,4,5-$C_6HF_4^•$	73.3	72.7
1,2,3,4,5-$C_6F_5^•$	78.3	78.0

[a] In kcal mol^{-1} energy unit.

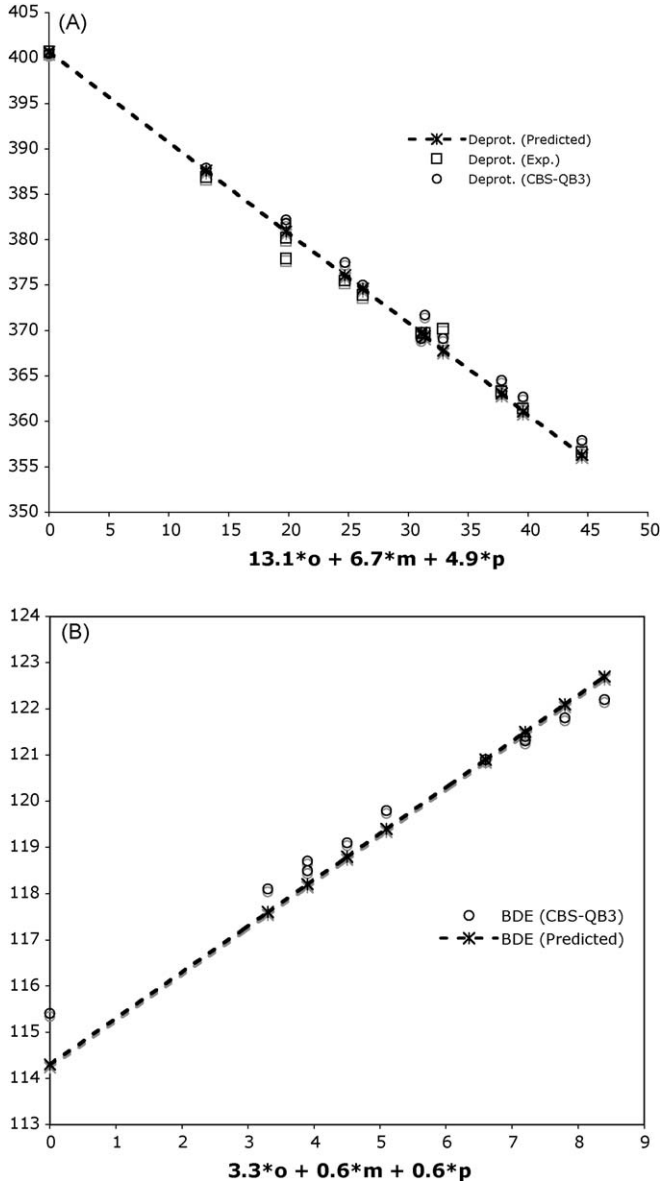


Fig. 2. Enthalpy of deprotonation (A) and bond dissociation energy (B) of compounds studied in the present work versus number of fluorine atoms at different positions (see Eqs. (3) and (4)). The circles are the CBS-QB3 calculated values; squares are available experimental data.

coefficients of *o*, *m* and *p*, it is seen that the deprotonation enthalpy shows a stronger dependence on the extent of fluorination than the homolytic BDEs. This is presumably because in the latter case the destabilizing effects of sigma withdrawal on the product radical are countered to some extent by the stabilizing effects of increasing lone pair donation.

4. Conclusions

High-level composite procedures are reliable for studying gas-phase acidities and deprotonation enthalpies of fluorinated compounds, and these methods can be applied in conjunction with lower-cost DFT geometries and frequencies. In particular, the high-level ab initio methods, G3//B3-LYP and CBS-QB3, are shown to reproduce experimental data to within an average of 1.9 and 1.4 kcal mol^{-1}, respectively. Lower-level procedures such as M05-2X and MP2 are also promising but should be used cautiously, as their accuracy is dependent on significant systematic error cancellation.

The acidity of benzene and its fluorinated derivatives is strongly influenced by the extent of fluorination and the substitution pattern. The acidities decrease strongly with proximity to sigma-withdrawing fluorine atoms due to their stabilizing effect on the product anion. In contrast to these heterolytic BDEs, the homolytic BDEs *increase* with increasing fluorination, reflecting the destabilizing effect of sigma withdrawal on the product radical which outweighs the stabilizing effects of lone pair donation. Both types of BDE can be fitted by simple linear formulae that depend only on the numbers of ortho, meta and para fluorine atoms present.

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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.jfluchem.2009.04.003.

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