Proton affinities of fluoro derivatives of benzene, toluene, and *m*-xylene from *ab initio* MP2 calculations

Yu. A. Borisov

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: yabor@ineos.ac.ru

The proton affinity (*PA*) energies of fluoro derivatives of benzene, toluene, and *m*-xylene were obtained from *ab initio* MP2-FC/6-31G* calculations and compared with experimental results. Protonated forms of the molecules, resulting from different ways of proton addition, were studied. Relative concentrations of isomeric arenonium ions were calculated and compared with the results of NMR studies on arenonium ions in solutions.

Key words: *ab initio* quantum-chemical calculations, MP2 method; fluoro derivatives of benzene, toluene, and *m*-xylene; proton affinity, isomeric arenonium ions, relative concentrations of isomers.

Investigation of the fundamental thermodynamic properties of protonated forms of organic compounds is an important phase of studies on proton transfer between molecules in the gas phase and in solution. There are three main methods for determination of the gas-phase proton affinity (*PA*) energies. The oldest, and most fundamental, method involves studies of the formation of ions under the action of either monoenergetic electron impact[1] or photoionization techniques.[2] The second method uses[3] measurements of the equilibrium constants for reversible proton transfer between two molecules B^1 and B^2:

$$B^1H^+ + B^2 \rightleftharpoons B^2H^+ + B^1.$$

The third, purely theoretical, approach is based[4,5] on quantum-chemical calculations of the enthalpies of protonation of the molecules, $B + H^+ = BH^+$. Currently, the *PA* energies obtained from *ab initio* calculations are almost as reliable as those determined experimentally. The best results are achieved by using those computational methods which take into account the energy of electron correlation in molecular systems (the MP2, MP4, CCSD(T) methods, *etc.*) and make use of rather large basis sets (the 6-31G*, 6-31++G*, aug-cc-pVDZ, aug-cc-pVTZ basis sets, *etc.*). Recent comparison of experimental *PA* energies with those obtained from calculations[6] at the G2 level of theory for a large number of molecules spanning a wide range of the *PA* scale (from H_2 to Me_2NH) showed that they differed by at most 2.5 kcal mol^{-1}.

Benzene derivatives behave[7] in strong acids as bases, which can add a proton to give salt-like compounds $A + HY = AH^+ + Y^-$ with arenonium ions AH^+ as the cationic fragments of the compounds. Previously, we have studied the structure of arenonium ions (AI) and the energetics of their isomeric transformations by semiempirical[8—10] and *ab initio*[11] quantum-chemical methods. For instance, *ab initio* MP2/6-31G* calculations of the molecular structures and energies of the AI of dichlorobenzenes for different ways of protonation have been carried out.[11] We found that the order of proton addition to different carbon atoms in dichlorobenzenes is similar to that predicted by the additivity schemes of substituent effects in *ortho-*, *meta-*, and *para*-positions. Proton migration in these AI is more energetically favorable than the migration of a Cl atom.

Experimental data on the *PA* energies of polyfluorobenzenes obtained by different authors[12] seem to be to some extent non-self-consistent. On the other hand, no high-level *ab initio* calculations of fluoro-substituted AI have been reported as yet. The aim of this work is to perform *ab initio* calculations of the neutral molecules and AI of benzene, toluene, *m*-xylene, and their fluorosubstituted derivatives, thus compensating for the lack of theoretical data.

Calculation Procedure

The MP2-FC calculations of the neutral molecules of benzene, toluene, *m*-xylene, as well as their fluoro-substituted and protonated forms were carried out using the GAUSSIAN-98 program package[13] with the 6-31G* basis set on a CRAY J-90 supercomputer (National Energy Research Supercomputer Center, Berkeley, California, USA). Stable configurations on the potential energy surface were located by full geometry optimization using analytical gradients.

As is known,[5] the size of a basis set affects the accuracy of calculations of the *PA* energies of small molecules in such a way that augmentation of the basis set with polarization functions (passage from the 6-31G* to 6-31G** basis set) changes the *PA* values by 2 to 3 kcal mol^{-1}.

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Results and Discussion

We performed calculations for all isomeric structures of the molecules of difluorobenzenes and their protonated forms. Relative stabilities of neutral difluorobenzenes decrease as follows: *meta*- > *para*- (0.63 kcal mol^{-1}) > *ortho*-isomer (4.14 kcal mol^{-1}). The relative energies are given in parentheses. The *meta*-isomer was found to be the most stable. The calculated data on the relative stabilities of these molecules are in good agreement with the experimental values of the relative energies (0.60 and 3.68 kcal mol^{-1}).[14]

Table 1. Calculated and experimental proton affinity energies of the molecules (PA_{theor} and PA_{exp}, respectively) and relative concentratiions of isomeric arenonium ions

Carbocation[a]	PA_{theor}	PA_{exp}[b]	C_{rel} (%)[c]
	kcal mol^{-1}		
1-H,$C_6H_6^+$ (**1**)	183.6	180.0, 181.3	100.0
1-F,1-H,$C_6H_5^+$ (**2**)	164.9	—	0.0
1-F,2-H,$C_6H_5^+$ (**3**)	183.1	—	0.5
1-F,3-H,$C_6H_5^+$ (**4**)	175.9	—	0.0
1-F,4-H,$C_6H_5^+$ (**5**)	186.4	181.3, 182.6	99.5
1,2-F_2,4-H,$C_6H_4^+$ (**6**)	178.5	175.7, 181.8	99.8
1,3-F_2,2-H,$C_6H_4^+$ (**7**)	181.8	—	0.3
1,3-F_2,4-H,$C_6H_4^+$ (**8**)	184.6	180.0, 181.9	99.7
1,4-F_2,2-H,$C_6H_4^+$ (**9**)	175.9	171.5, 181.2	100.0
1,2,3-F_3,4-H,$C_6H_3^+$ (**10**)	177.5	173.0	100.0
1,2,3-F_3,5-H,$C_6H_3^+$ (**11**)	171.6	—	0.0
1,2,4-F_3,3-H,$C_6H_3^+$ (**12**)	174.4	—	0.1
1,2,4-F_3,5-H,$C_6H_3^+$ (**13**)	178.4	174.5, 181.4	99.9
1,2,4-F_3,6-H,$C_6H_3^+$ (**14**)	168.5	—	0.0
1,3,5-F_3,2-H,$C_6H_3^+$ (**15**)	183.1	178.4, 181.0	100.0
1,2,3,4-F_4,5-H,$C_6H_2^+$ (**16**)	168.9	165.8, 181.1	100.0
1,2,4,5-F_4,3-H,$C_6H_2^+$ (**17**)	167.3	—	100.0
1,2,3,4,5-F_5,6-H,C_6H^+ (**18**)	169.9	164.3, 179.9	100.0
$C_6F_6H^+$ (**19**)	157.7	—	100.0
1-Me,1-H,$C_6H_5^+$ (**20**)	183.5	—	0.0 (0.0)
1-Me,2-H,$C_6H_5^+$ (**21**)	190.1	—	24.0 (25.0)
1-Me,3-H,$C_6H_5^+$ (**22**)	186.5	—	0.0 (0.0)
1-Me,4-H,$C_6H_5^+$ (**23**)	191.1	187.7, 189.8	75.9 (75.0)
1-Me,3-F,2-H,$C_6H_4^+$ (**24**)	189.2	—	0.7 (0.0)
1-Me,3-F,4-H,$C_6H_4^+$ (**25**)	190.7	—	11.5 (11.6)
1-Me,3-F,5-H,$C_6H_4^+$ (**26**)	179.2	—	0.0 (0.0)
1-Me,3-F,6-H,$C_6H_4^+$ (**27**)	191.8	—	87.7 (88.5)
1,3-Me_2,2-H,$C_6H_4^+$ (**28**)	196.0	—	5.3
1,3-Me_2,4-H,$C_6H_4^+$ (**29**)	197.2	—	94.7
1,3-Me_2,5-H,$C_6H_4^+$ (**30**)	189.2	—	0.0
1,3-Me_2,5-F,2-H,$C_6H_3^+$ (**31**)	197.7	—	90.2 (83.5)
1,3-Me_2,5-F,4-H,$C_6H_3^+$ (**32**)	196.2	—	9.8 (16.4)

[a] Formed upon proton addition to molecule.

[b] The first value in the column was taken from Ref. 12 and the second value was taken from the database of the gas-phase proton affinities of molecules.[23]

[c] Relative concentration of isomeric ion: experimental values obtained from the results of NMR studies[20–22] are given in parentheses.

The *PA* energies were calculated as differences between the calculated total energies of neutral molecules and the corresponding protonated forms (Table 1). Comparison of calculated and experimental *PA* energies (PA_{theor} and PA_{exp}, respectively) for a set of molecules (Fig. 1) shows that curve *1* corresponding to the PA_{theor} values passes ~4 kcal mol^{-1} above curve *2* for PA_{exp}. Qualitatively, both curves have a similar shape.

Assuming that different isomeric arenonium ions are in thermodynamic equilibrium, we can determine their ratio in the gas phase. To this end, the Boltzmann distribution for the relative concentrations of isomers, C_k, should be used:

$$C_k = \exp[-\Delta G_k^\circ/(RT)]/\sum_i n_i \exp[-\Delta G_i^\circ/(RT)], \qquad (1)$$

where $\Delta G_i^\circ = \Delta H_i^\circ - T\Delta S_i^\circ$. Here, ΔG_i°, ΔH_i°, and ΔS_i° are the changes in the Gibbs free energy, enthalpy, and entropy, respectively; *k* is the number of the position for protonation; *i* is the running number of the inequivalent position for protonation; and *n* is the number of symmetric, energetically equivalent positions for protonation of a molecule. According to the published data,[15–19] the protonation entropies of aromatic hydrocarbons and their derivatives depend only slightly on their structure and basicity. Our MP2/6-31G* calculations of the thermodynamic functions for the isomeric arenonium ions of fluorobenzene showed that the changes in the entropy contributions on going from one isomer to another are less than 5% and do not alter the order of changes in the

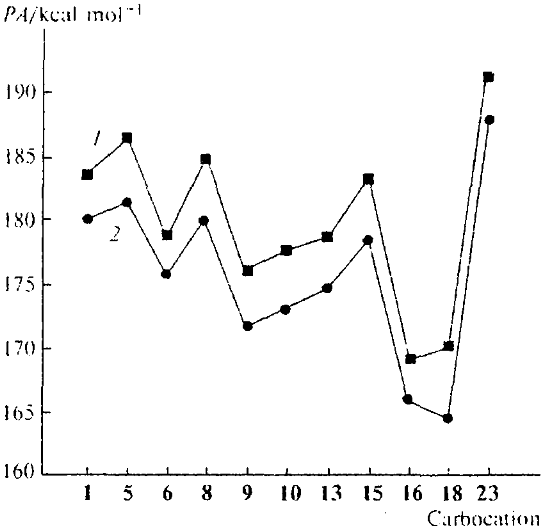

Fig. 1. Comparison of calculated (*1*) and experimental (*2*) *PA* energies. The numbering of carbocations corresponds to that given in Table 1.

stability of the arenonium ions. Therefore, the ratio of isomeric forms of arenonium ions is mainly determined by the enthalpy difference, *i.e.*, by the relationship

$$C_k = \exp[-\Delta H_k^\circ/(RT)]/\sum_i n_i \exp[-\Delta H_i^\circ/(RT)]. \qquad (2)$$

The concentrations of isomeric arenonium ions calculated using expression (2) and the experimental values obtained from the NMR spectra of the corresponding arenonium ions in solution[20—22] are listed in Table 1.

Summing up, in this work we calculated the *PA* energies for a number of fluoro derivatives of benzene, toluene, and *m*-xylene for different types of proton addition. The relative concentrations of arenonium ions of all compounds were also determined.

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