Comparative semiempirical, ab initio, and density functional theory study on the thermodynamic properties of linear and branched perfluoroalkyl sulfonic acids/sulfonyl fluorides, perfluoroalkyl carboxylic acid/acyl fluorides, and perhydroalkyl sulfonic acids, alkanes, and alcohols

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Abstract

A systematic and comprehensive semiempirical, Hartree-Fock (HF) ab initio, and B3LYP density functional theory (DFT) study was conducted on the relative thermodynamic properties of various linear and branched perfluorinated and perhydrogenated alkyl compounds. The semiempirical AM1, PM3, and PM6 methods all consistently and accurately predict that branched alkyl compounds will generally be more thermodynamically stable than their linear counterparts. In contrast, HF and B3LYP calculations with the 6-31G(d,p), 6-31++G(d,p), and 6-311++G(d,p) basis sets predict that linear isomers will be more stable than branched analogs. These different linear versus branched perfluoroalkyl/perhydroalkyl thermodynamic property trends between semiempirical and ab initio/DFT methods were evident in both gas and aqueous phase calculations. Comparison of experimentally determined thermodynamic properties for several classes of linear and branched alkanes and alcohols with values calculated at the PM6 and B3LYP/6-31++G(d,p) levels of theory supported the well known findings that such DFT and HF approaches incorrectly predict branched alkyl compounds will be less thermodynamically stable than linear isomers. Calculations at the MP2/6-311++G(d,p)/B3LYP/6-311++G(d,p) and M05-2X/6-311++G(d,p) levels of theory on a representative subset of the linear and branched perfluorinated compounds supported the thermodynamic conclusions from the PM6 method. Strong agreement between PM6 estimated thermodynamic properties and available experimental data supports use of this computational method for accurately calculating the well established higher thermodynamic stability of branched alkyl compounds. Branched perfluoroalkyl compounds are thus expected to be more thermodynamically stable than their linear analogs.
Keywords: Perfluoroalkyl compounds; Sulfonic acids; Sulfonyl fluorides; Carboxylic acids; Acyl fluorides; Alkanes; Alcohols; Thermodynamic properties; Alkyl chain branching
1. Introduction

Perfluoroalkyl sulfonic acids (PFSAs) are widely used in commercial activities and products [1] and have become globally distributed contaminants over the past several decades with a range of toxicological issues.[2] The physicochemical properties of these compounds are difficult both to experimentally determine and to estimate via computational methods [3]. Among the various PFSA properties under study, such as acid dissociation constants [4,5] and various partitioning coefficients,[3,6,7] the thermodynamic properties are of current interest due to their utility in estimating the energy profiles for degradation methods, their applications in calculating partitioning behavior, and their potential utility in predicting the presence and relative abundance of new PFSA isomers in technical mixtures and environmental samples [8-10]. In the absence of experimental data, which is understood given the expense, difficulty, and number of individual isomers in longer perfluoroalkyl chain homologues,[11] previous efforts have focused on calculating the thermodynamic properties of PFSAs such as n-perfluorooctane sulfonic acid (n-PFOS) and its branched isomers [10,12,13].

However, differences have emerged between semiempirical [10] and B3LYP density functional theory (DFT) [12,13] approaches for estimating the relative free energies of linear and branched long-chain PFSAs. Whereas the semiempirical PM6 method generally predicts a decrease in gas phase thermodynamic stability with increasing linearity of the perfluoroalkyl chain,[10] DFT calculations at the B3LYP/6-31++G(d,p) level have suggested that the linear n-PFOS isomer is more thermodynamically stable than its monomethyl branched counterparts [12,13]. These different computational results have led to disagreements regarding the potential usefulness of
relating computationally derived thermodynamic properties (e.g., Gibbs free energies) for PFSAs to their reported abundances in technical mixtures, and also raise concerns as to which level of calculation is generally best employed to study the environmental fate of these compounds. To help resolve these issues, we have undertaken a systematic and comprehensive investigation into the thermodynamic properties of linear and branched perfluoroalkyl sulfonic acids, sulfonyle fluorides, carboxylic acids, and acyl fluorides, and perhydroalkyl sulfonic acids, alkanes, and alcohols at various semiempirical, ab initio, and DFT levels of theory.

2. Computational details

Semiempirical AM1,[14] PM3,[15] and PM6 [16] calculations, and Hartree-Fock ab initio and B3LYP [17,18] and M05-2X [19] density functional theory (DFT) calculations using the 6-31G(d,p), 6-31++G(d,p), and 6-311++G(d,p) basis sets,[20-32] were conducted using Gaussian 09 [33] with the high-performance computing resources on the Western Canada Research Grid (WestGrid; project #100185; K. Forest) and the Shared Hierarchical Academic Research Computing Network (SHARCNET; project #sn4612; K. Forest). MP2 [34-39] single point calculations were conducted at the MP2/6-31+G(d,p)//B3LYP/6-31+G(d,p) and MP2/6-311++G(d,p)//B3LYP/6-311++(d,p) levels. All calculations used the same gas phase starting geometries obtained via the PM6 semiempirical method [16] as employed in MOPAC 2009 (http://www.openmopac.net/; v. 9.099). Aqueous phase calculations in Gaussian 09 employed the polarizable continuum model (PCM) [40] for both geometry optimizations and frequency calculations. All optimized structures were confirmed as true minima by vibrational analysis at the same level.
3. Results and discussion

Gas phase calculations for the linear perfluorooctane sulfonic acid (n-PFOS; \(C_8\) PFSA 89) and its six monomethyl branched isomers (1- through 6-CF\(_3\)-PFOS; \(C_8\) PFSAs 83 through 88) (Fig. 1) using the semiempirical AM1, PM3, and PM6 methods and Hartree-Fock (HF) ab initio and B3LYP density functional theory (DFT) calculations using the 6-31G(d,p), 6-31G++(d,p), and 6-311G++(d,p) basis sets indicate computational method dependent relative Gibbs free energy thermodynamic stability rankings for these compounds (Table 1). With the exception of the PM3 method, all semiempirical, HF, and DFT calculations conducted indicate that 1-CF\(_3\)-PFOS (\(C_8\) PFSA 83) is the most thermodynamically stable gas phase isomer among this selected subset of PFOS isomers, but the relative Gibbs free energy rankings of the other six isomers vary widely between computational approaches. In comparison, the PM3 method predicts 6-CF\(_3\)-PFOS (\(C_8\) PFSA 88) to be the most thermodynamically stable of the seven isomers, with 1-CF\(_3\)-PFOS as only the fifth most stable isomer having a gas phase Gibbs free energy 4.9 kJ mol\(^{-1}\) higher than for 6-CF\(_3\)-PFOS. At the B3LYP/6-31++G(d,p) level, our results are in approximate qualitative agreement with the recent findings of Torres et al. [13]. However, these authors reported that the acid form of n-PFOS had the lowest Gibbs free energy among the seven isomers under consideration, with a \(\Delta G_{(g)}^{\circ}\) of +1.4 kJ mol\(^{-1}\) between n-PFOS (\(G_{(g)}^{\circ}=-2626.506224\) H [\(\text{H=hartrees}\)]) and 1-CF\(_3\)-PFOS (\(G_{(g)}^{\circ}=-2626.505673\) H), respectively. In contrast, we find that the molecular form of gas phase n-PFOS (\(G_{(g)}^{\circ}=-2626.526092\) H) is 0.3 kJ mol\(^{-1}\) less stable (i.e., a \(\Delta \Delta G_{(g)}^{\circ}\) difference of 1.7 kJ mol\(^{-1}\) compared to Torres et al. [13]) than 1-CF\(_3\)-PFOS (\(G_{(g)}^{\circ}=-2626.526222\) H) at the B3LYP/6-31++G(d,p) level.
Using the PM6 method in MOPAC 2007 (data taken from our previous work in ref. [10]) and Gaussian 09 (current work), linear n-PFOS is predicted to be either the least thermodynamically stable (MOPAC 2007) or second-least stable (Gaussian 09) among these seven isomers. Similarly, the PM3 method predicts that n-PFOS will be the least stable, while the AM1 method predicts a ranking of fourth most stable. Using the HF and B3LYP methods, the relative stability ranking of n-PFOS among these seven isomers increases in stability with increasing level of basis set theory. The linear isomer is predicted to be the third and fourth most thermodynamically stable of these seven selected isomers with the 6-31G(d,p) basis set and the HF and B3LYP methods, respectively, thereafter increasing to the second most stable isomer with the 6-31++G(d,p) and 6-311++G(d,p) basis sets under both methods, respectively. These differences in Gibbs free energy rankings between computational methods are primarily due to how each method treats the enthalpy of linear versus monomethyl branched perfluoroalkyl chains. As shown in Table S1 of the Supplementary Material, enthalpic contributions toward the Gibbs free energy play a dominant role in determining the relative thermodynamic stability of these seven PFOS isomers, with comparatively minor contributions from the relative entropies of each compound, similar to the discussions put forward by Torres et al. [13] in their gas phase B3LYP/6-31++G(d,p) study on the acid, anion, and lithium and sodium salts of these compounds.

However, for computationally derived free energies to be of value in comparison to observed PFOS technical mixture isomer profiles, the following two criteria must be rigorously met. Among all the 89 individual linear and branched PFOS isomers [11] (not just a selection of the
linear and its six monomethyl isomers, as has been proposed [12,13]), the order of prevalence in
technical mixtures must match the relative order of thermodynamic stabilities predicted by the
computational approach. In addition, for a quantitative treatment of the problem, the relative
prevalence (i.e., molar ratios) of the various PFOS isomers identified in technical mixtures must
obey a Boltzmann distribution as calculated from the ΔG values. With a Boltzmann distribution,
even small values of ΔG (i.e., several kJ mol⁻¹) will result in large differences between the
calculated contributions of various isomers. As we have previously discussed,[10,41] neither of
these criteria can be met either qualitatively or quantitatively with the existing computational
data at any level of theory (be it semiempirical, ab initio, or DFT) and the published suite of
studies [12,26-31] on the isomer compositions of PFOS technical mixtures.

Furthermore, PFOS technical mixtures were synthesized using the electrochemical fluorination
(ECF) approach in hydrofluoric acid using linear perhydrogenated n-octane sulfonyl fluoride
starting material, which yielded perfluoroalkyl sulfonyl fluorides (PFSFs), not PFSAs, as the
primary products for which chain rearrangements would have been occurring. Following
production of the PFSFs, these compounds were either hydrolyzed (a process expected to be
quantitative for all isomers, and not expected to display any isomer discrimination) to yield the
PFSA technical mixtures, or derivatized to other commercial products such as perfluoroalkyl
sulfonamides and related compounds [1,48]. As such, for a rigorous thermodynamic
investigation of PFOS technical mixtures, the computationally derived thermodynamic
comparison should ideally be made for the PFSFs using a hydrofluoric acid solvent model.

As with the linear and monomethyl branched PFOS isomers, we conducted analogous
semiempirical, HF, and DFT gas phase calculations on the corresponding linear and monomethyl branched perfluorooctane sulfonyl fluoride (PFOSF) isomers (Table 2). The gas phase computational investigation of these PFOSF isomers supports the PFOS calculations, whereby the 1-CF3-PFOSF isomer is predicted to be the most thermodynamically stable under all methods (except for the PM3 method, which predicts 6-CF3-PFOSF to have the lowest Gibbs free energy among these seven compounds). In addition, the PFOSF isomer calculations, as with the PFOS isomers, also indicated that the linear congener is predicted to be among the least stable of the congeners using semiempirical methods, but achieves progressively higher relative thermodynamical stability with higher level basis sets under the HF and DFT approaches, maximizing as the second most stable isomer with the 6-31++G(d,p) and 6-311++G(d,p) basis sets.

In the absence of a well-established computational solvent approximation for hydrofluoric acid, we also conducted both PCM-PM6 and PCM-B3LYP/6-311++G(d,p) calculations on the seven linear and monomethyl branched PFOS and PFOSF isomers in water (Table 3). The results are similar to the gas phase calculations, with n-PFOS/F and 1-CF3-PFOS/F being of about equal thermodynamic stability at the PCM-B3LYP/6-311++G(d,p) level versus 1-CF3-PFOS/F being clearly the most stable isomer at the PCM-PM6 level, 6-CF3-PFOS being moderately less stable than n-PFOS/F and 1-CF3-PFOS/F at the PCM-B3LYP/6-311++G(d,p) level and being clearly the second most stable isomer at the PCM-PM6 level, and 2- through 5-CF3-PFOS/F consistently having the lowest thermodynamic stabilities across both computational approaches and compound classes. Thus, consistent with our previous analyses and the available experimental datasets, no currently available gas or aqueous phase level of computation on the linear and
monomethyl branched PFOS or PFOSF isomers either qualitatively or quantitatively reproduces the varied multi-isomer patterns reported to exist in technical PFOS mixtures.

To further probe the potential for either the semiempirical PM6 or the B3LYP/6-311++G(d,p) DFT methods to predict the isomer distributions in technical PFSA mixtures, we performed gas phase calculations on the molecular forms of all 159 C₃ through C₈ branched and linear PFSA isomers using each of these two levels of theory (Fig. 2 and Supplementary Material Table S2). We have also included for comparison in Figure 2 our previously published ΔG°(g) data using the THERMO function for PM6 in MOPAC 2007 [10]. There is excellent agreement between the PM6 ΔG°(g) values we previously obtained [10] using MOPAC 2007 and the current results with zero point energy and thermal corrections using Gaussian 09 (average signed difference=-3.2 kJ mol⁻¹; average unsigned difference=4.6 kJ mol⁻¹; root mean squared difference=5.7 kJ mol⁻¹; ΔG°(g)PM6,Gaussian 09=0.95 × ΔG°(g)PM6,MOPAC 2007 – 0.31 for all congeners across the C₃ through C₈ homologues; r=0.984).

Whereas the PM6 method generally predicts increasing PFSA thermodynamic stability with increased branching for all C₃ through C₈ homologues, the B3LYP/6-311++G(d,p) calculations clearly indicate increasing stability with increased linearity of the perfluoroalkyl chain within each homologue group at perfluoroalkyl chain lengths of C₆ and higher. This B3LYP/6-311++G(d,p) chain linearity-thermodynamic stability trend becomes more pronounced within each homologue group as the chain length increases (particularly at ≥C₆). For the shorter chain PFSAs (i.e., C₃ and C₄), both the PM6 and B3LYP/6-311++G(d,p) calculations are in agreement, indicating that the linear members of each homologue (i.e., n-propyl and n-butyl) are less
thermodynamically stable than their branched counterparts. Within the C5 (pentyl) PFSA homologue, differences in the relative thermodynamic stability ranking of these two computational methods begin to be displayed, with the PM6 method predicting the n-pentyl PFSA to be the least stable among the eight isomers, whereas the B3LYP/6-311++G(d,p) level of theory predicts this linear congener will be the fourth most stable. For the C6, C7, and C8 homologues, the relative thermodynamic stability ranks for the linear members under each level of theory are as follows: C6, PM6=16/17, B3LYP/6-311++G(d,p)=3/16; C7, PM6=32/39, B3LYP/6-311++G(d,p)=5/39; and C8, PM6=55/89, B3LYP/6-311++G(d,p)=6/89.

As such, we identified these increasingly deviant linear versus branched thermodynamic stability trendings at the ≥C5 perfluoroalkyl homologues between the PM6 and B3LYP/6-311++G(d,p) levels of theory as representing fundamental differences between the two computational methods that were worthy of further investigation, as is discussed in more detail below. In addition, whereas the PM6 method in Gaussian 09 predicts that n-PFOS will have a $\Delta G_{(g)}^\circ$ rank of 55 among the 89 PFOS isomers (c.f., MOPAC 2007 predicts a corresponding rank of 71 [10]), the B3LYP/6-311++G(d,p) calculations predict that n-PFOS will have a $\Delta G_{(g)}^\circ$ rank of 6. This result is significant in that, even at the B3LYP/6-311++G(d,p) level of theory, n-PFOS is not the most thermodynamically stable isomer among the 89 possible C8 congeners. The B3LYP/6-311++G(d,p) gas phase calculations still predict that the 1,1-dimethylhexyl (C8 PFSA 68; $G_{(g)}^\circ=-2627.149433$ H; $\Delta G_{(g)}^\circ=0.0$ kJ mol$^{-1}$), 5,5'-dimethylhexyl (C8 PFSA 82; $G_{(g)}^\circ=-2627.148640$ H; $\Delta G_{(g)}^\circ=+2.1$ kJ mol$^{-1}$), 1,4,4'-trimethylpentyl (C8 PFSA 54; $G_{(g)}^\circ=-2627.148376$ H; $\Delta G_{(g)}^\circ=+2.8$ kJ mol$^{-1}$), 1,1',4-trimethylpentyl (C8 PFSA 48; $G_{(g)}^\circ=-2627.147817$ H; $\Delta G_{(g)}^\circ=+4.2$ kJ mol$^{-1}$), and 1-methylheptyl (C8 PFSA 83; $G_{(g)}^\circ=-2627.143643$ H; $\Delta G_{(g)}^\circ=+15.2$ kJ mol$^{-1}$) substituted
congeners will all be more thermodynamically stable than the linear n-PFOS (C₈ PFSA 89; G(\theta)°=-2627.142967 H; ΔG(\theta)°=+17.0 kJ mol⁻¹). These stability rankings were confirmed for condensed phase calculations at the PCM-B3LYP/6-311++G(d,p) level in water, whereby in this solvent model, C₈ PFSA 82 (G(\theta)°=-2627.160041 H; ΔG(\theta)°=0.0 kJ mol⁻¹), C₈ PFSA 68 (G(\theta)°=-2627.159633 H; ΔG(\theta)°=+1.0 kJ mol⁻¹), C₈ PFSA 54 (G(\theta)°=-2627.15903 H; ΔG(\theta)°=+2.7 kJ mol⁻¹), and C₈ PFSA 48 (G(\theta)°=-2627.157218 H; ΔG(\theta)°=+7.4 kJ mol⁻¹) are still all significantly more thermodynamically stable than n-PFOS (G(\theta)°=-2627.154633 H; ΔG(\theta)°=+14.2 kJ mol⁻¹). Thus, if the synthesis of technical PFOS mixtures were under thermodynamic control, and computationally derived gas or aqueous phase relative thermodynamic stabilities for the acid forms were to be of utility in either qualitatively or quantitatively predicting the isomeric composition of these mixtures, both the PM6 and B3LYP/6-311++G(d,p) levels of theory predict that n-PFOS should be a minor isomeric contributor, with at least several other branched compounds being significantly more thermodynamically stable than the linear congener.

To determine if these relative thermodynamic property differences between the semiempirical, ab initio, and DFT calculations were due to substantial differences in the optimized geometries obtained for linear n-PFOS among the various levels of theory, we compared the optimized geometrical features (bond lengths and angles) obtained for this compound using the PM6, HF/6-311++G(d,p), and B3LYP/6-311++G(d,p) methods with the reported crystal structure experimental data on the perfluoroalkyl chain of N-ethylperfluorooctane sulfonamide (Table 4 and Fig. 3). Excellent agreement between the experimental and calculated geometries was obtained using all three methods, with the following root mean squared errors in bond lengths and angles: bond lengths, PM6=0.0149 Å, HF/6-311++G(d,p)=0.0212 Å, B3LYP/6-
311++G(d,p)=0.0156 Å; bond angles, PM6=1.5°, HF/6-311++G(d,p)=0.8°, B3LYP/6-311++G(d,p)=0.7°. The average distance between neighboring fluorine atoms on the perfluoroalkyl chain was equivalent at between 2.74 to 2.75 Å for the PM6 and B3LYP/6-311++G(d,p) methods. A smaller twist angle (defined as the average FCCF dihedral along the perfluorocarbon chain) of between 11.5 to 12.5° was found using the PM6 method compare to a corresponding range of 16.5 to 17.5° at the B3LYP/6-311++G(d,p) level (see axial views in Fig. 3 for a visual representation of the method differences).

Thus, in a number of cases, the PM6 bond length and angle estimates for the linear PFOS were found to be superior to both the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) estimates, suggesting a lack of obvious significant and fundamental bias and/or substantial inferiority of the PM6 geometry versus the ab initio and DFT calculations. In addition, there appeared to be only a modest difference in the geometries of the 1-CF₃-PFOS between the PM6 and B3LYP/6-311++G(d,p) calculations, perhaps insufficient to satisfactorily explain the large ΔΔG(°) of 17.9 kJ mol⁻¹ between n-PFOS and 1-CF₃-PFOS for these two methods (i.e., ΔG(°) of 19.7 kJ mol⁻¹ at the PM6 level and 1.8 kJ mol⁻¹ at the B3LYP/6-311++G(d,p) level relative to the most stable of the seven linear and monomethyl branched isomers in each method). For example, the 1-CF₃-PFOS, C₁-Cₘethyl bond lengths between the α-carbon on the perfluoroalkyl chain and the carbon on the perfluoromethyl substituent were 1.5371 Å (PM6) and 1.5634 Å (B3LYP/6-311++G(d,p)), the C₂-C₁-Cₘethyl bond angles were 117.2° (PM6) and 116.4° (B3LYP/6-311++G(d,p)), and the minimum distance between the C₁ fluorine and any of the perfluoromethyl substituent fluorines was 2.6613 Å (PM6) and 2.6703 Å (B3LYP/6-311++G(d,p)). Similar twist angles were observed using these two methods for 1-CF₃-PFOS as for the linear isomer. We therefore sought to
examine whether the perfluorination of the octyl chain was the cause of these substantial thermodynamic property differences between the PM6 and B3LYP/6-311++G(d,p) methods, since it has been previously suggested that semiempirical methods do not properly account for the electrostatic repulsion between adjacent fluorine atoms on a perfluoroalkyl chain [13,49].

For example, Zhang and Lerner reported a nearly eclipsed chain geometry for the n-PFOS anion using the semiempirical PM3 method as employed in Gaussian 94 [49]. The cause of this eclipsed n-PFOS anion perfluoroalkyl chain geometry at the PM3 level is difficult to determine a decade later, but we cannot reproduce this purported global minimum using either the PM3 method as implemented in MOPAC 2000, or as implemented in either Gaussian 03 or Gaussian 09. Using each of these three software programs, we find the PM3 method yields a helical perfluoroalkyl geometry for both the acid and anion forms of n-PFOS, with an average twist angle range of between 17 to 19°. It is clear from our experience, however, that under some initial starting geometries where the perfluoroalkyl chain is PM3 geometry minimized from a prior eclipsed conformation molecular mechanics (e.g., MM2 [50]) minimization effort, the PM3 method may find a local minimum having an eclipsed geometry with a $\Delta H_{(g)}$ about 25 to 26 kJ mol$^{-1}$ higher than that of the global minimum helical geometry (Fig. 4). This higher energy eclipsed local minimum for the PM3 method can readily be avoided by inserting a slight perturbation in a FCCF dihedral angle prior to the PM3 geometry optimization, after which it appears the PM3 method will always optimize to the expected helical global minimum whose geometrical parameters agree very well with ab initio and DFT calculations.

Similarly, Erkoc and Erkoc reported a helical perfluoroalkyl geometry using the semiempirical
AM1 method for the n-PFOS acid, although the n-PFOS anion (lithium salt) was reported to have a nearly eclipsed perfluoroalkyl conformation [51]. Similar to these authors, we also found bond lengths of about 1.61 Å between adjacent perfluorocarbons for n-PFOS acid using the AM1 method in MOPAC 2000. However, we obtained correspondingly consistent carbon-fluorine bond lengths of about 1.37 Å, and no C-F bond lengths near the lower end of the 1.32 to 1.37 Å range reported in this prior study. The carbon-sulfur bond length of 4.463 Å reported by Erkoc and Erkoc for the n-PFOS acid is clearly in error, as we obtain a value of 1.938 Å that is consistent with covalent bonding expectations. We also cannot reproduce the nearly eclipsed perfluoroalkyl chain reported by these authors for the n-PFOS anion using the AM1 method as implemented either in MOPAC 2000, Gaussian 03, or Gaussian 09, either with or without the lithium countercation. The AM1 method in any of these programs yields a helical global minimum geometry for both the acid and anion (both with and without a lithium countercation) forms of n-PFOS. We also obtained a ΔHf(g)° of -933.6 kcal mol⁻¹ for the n-PFOS acid using a restricted wavefunction via the AM1 method in MOPAC 2000, much lower than the value of -888 kcal mol⁻¹ reported by Erkoc and Erkoc [35]. These authors used unrestricted Hartree-Fock (UHF) formalisms within the AM1 method and assumed that the ground state multiplicity of n-PFOS was as a triplet, rather than its actual singlet ground state multiplicity, likely explaining the unoptimized ground state geometry and energy they reported.

As a result, it appears that the AM1, PM3, and PM6 semiempirical methods as implemented in MOPAC 2000, Gaussian 03, and Gaussian 09 all yield ground state singlet helical conformations of the perfluoroalkyl chain for the acid and anion/anion salt forms of n-PFOS provided an appropriate search for the global minimum is undertaken. Similarly, both HF ab initio and
B3LYP DFT calculations also give helical perfluoroalkyl conformations with the 6-31G(d,p), 6-31++G(d,p), and 6-311++G(d,p) basis sets. However, it appears unclear which method provides the best approximation of the overall geometry for subsequent thermochemical calculations. An experimental twist angle of 12° is known for poly(tetrafluoroethylene) at between 19 to 30°C (phase IV; the twist angle increases to 14° at temperatures <19°C),[52,53] which is in good agreement with the PM6 (~12°) and AM1 (~12°) estimates, and lower than the PM3 (~17°), HF/6-31G(d,p) (~17°), HF/6-31++G(d,p) (~17°), HF/6-311++G(d,p) (~17°), B3LYP/6-31G(d,p) (~17°), B3LYP/6-31++G(d,p) (~17°), and B3LYP/6-311++G(d,p) (~17°) estimates from methods as implemented in Gaussian 09. Previous computational semiempirical, ab initio, and DFT studies on helicity of perfluoroalkyl chains also support our method dependent range of results [13,49,51,54-66].

Gas phase PM6 and B3LYP/6-311++G(d,p) calculations were then conducted on all 159 C₃ through C₈ perhydrogenated alkyl sulfonic acids to further our systematic study of the relative thermodynamic property differences between these two methods (Fig. 5 and Supplementary Material Table S3). As with the perfluoroalkyl analogs, the B3LYP/6-311++G(d,p) level of theory predicts that more linear isomers within each homologue group will be the most thermodynamically stable. A similar, but much weaker, trend has emerged for the PM6 method, with the comparative stability rankings for the linear member of each homologue as follows: C₃, PM6, 1/2, B3LYP/6-311++G(d,p), 2/2; C₄, PM6, 3/4, B3LYP/6-311++G(d,p), 3/4; C₅, PM6, 5/8, B3LYP/6-311++G(d,p), 1/8; C₆, PM6, 9/17, B3LYP/6-311++G(d,p), 3/17; C₇, PM6, 16/39, B3LYP/6-311++G(d,p), 3/39; and C₈, PM6, 27/89, B3LYP/6-311++G(d,p), 3/89. For the alkyl sulfonic acids, the PM6 method still only exhibits an intermediate thermodynamic stability rank.
for the linear congener within each homologue, whereas the B3LYP/6-311++G(d,p) predicts that the linear congener will be the most stable for the C5 homologue, and the third most stable for the C6, C7, and C8 homologues. For both the PM6 and B3LYP/6-311++G(d,p) level calculations, both methods yield optimized geometries with equivalent eclipsed conformation -CH2- moieties for all linear perhydroalkyl chains, consistent with experimental evidence (and in contrast to the experimentally known helical geometries of linear perfluoroalkyl chains). Consequently, even in the absence of fluorination, a fundamental difference remains in the relative thermodynamic stabilities of alkyl sulfonic acid isomers between semiempirical and DFT methods.

As was discussed above, the differences in how the semiempirical, ab initio, and DFT methods treat the free energies of perfluoro- and perhydro-alkyl chains is largely determined by variations in how each level of theory calculates the enthalpy of the respective alkyl chains. With the comparative thermodynamic property differences between the PM6 and B3LYP/6-311++G(d,p) levels of theory remaining as we moved from perfluoroalkyl sulfonic to perhydroalkyl sulfonic acids, our final choice of study was to investigate how well gas phase predictions from these two methods compared to established experimental values on the enthalpies of formation for linear and branched alkanes and alcohols (Table 5). The semiempirical PM6 method outperforms the B3LYP/6-311++G(d,p) calculations on these sets of benchmark compounds both in terms of the quantitative $\Delta H_{(g)}^\circ$ predictions and the qualitative relative thermodynamic stability rank order prediction. For the linear and branched butanols, pentanes, and pentanols, the PM6 and B3LYP/6-311++G(d,p) are in excellent rank order agreement, correctly predicting the enthalpic rank order for all butanols and the three pentanes under study, and having near equivalent rank RMSEs of 1.1 and 0.9, respectively, for the pentanols. The PM6 method outperforms the
B3LYP/6-311++G(d,p) calculations in estimating $\Delta H_g^\circ$ values within each of these three classes, however, having RMSEs of 4.3, 1.7, and 4.6 kJ mol$^{-1}$ for the butanols, pentanes, and pentanols, respectively, that are substantially lower than the corresponding B3LYP/6-311++G(d,p) RMSEs of 5.3, 8.5, and 7.0 kJ mol$^{-1}$.

As with the perfluorinated and perhydrogenated alkyl sulfonic acids, the deviation in thermodynamic property patterns between these two methods becomes most evident between the C$_5$ and C$_6$ homologues. For example, while the PM6 method correctly predicts the enthalpic rank order for all five hexane isomers examined, the B3LYP/6-311++G(d,p) method performs poorly, having a rank RMSE of 2.4. Similarly, the corresponding $\Delta H_g^\circ$ RMSE for the PM6 method (2.5 kJ mol$^{-1}$) is much lower than the corresponding B3LYP/6-311++G(d,p) RMSE (10.7 kJ mol$^{-1}$) for hexanes. The PM6 method, as with the butanols, pentanes, and pentanols, correctly predicts that the linear n-hexane will be the least thermodynamically stable isomer. In contrast, the B3LYP/6-311++G(d,p) method predicts this compound will be the most thermodynamically stable among the five isomers examined. With the nine linear and branched heptane isomers investigated, the PM6 method performs well both in terms of the rank order (RMSE=0.9) and the $\Delta H_g^\circ$ (RMSE=3.0 kJ mol$^{-1}$), in comparison to much lower accuracy for the B3LYP/6-311++G(d,p) method (rank RMSE=3.8; $\Delta H_g^\circ$ RMSE=9.0 kJ mol$^{-1}$). Again, the B3LYP/6-311++G(d,p) level of theory predicts that n-heptane will be the most thermodynamically stable isomer, in contrast to the experimental data that indicates it will be the least thermodynamically stable (in good agreement with the PM6 prediction of n-heptane being the second least stable isomer).
Analogous findings were obtained for the 18 octane isomers studied, with superior PM6 agreement with experimental data both in terms of the relative thermodynamic stability rank (RMSE=3.3) and the $\Delta H_{(g)}^{\circ}$ (RMSE=6.0 kJ mol$^{-1}$) compared to the B3LYP/6-311++G(d,p) results (rank RMSE=7.4; $\Delta H_{(g)}^{\circ}$ RMSE=12.2 kJ mol$^{-1}$). The PM6 method correctly predicted that the highly branched 2,2,3,3-tetramethylbutane isomer is the most thermodynamically stable, while the B3LYP/6-311++G(d,p) calculations predicted this isomer would have a stability rank of 15/18. Similar to the hexanes, heptanes, and perfluoroalkyl and perhydroalkyl sulfonic acids and perfluoralkyl sulfonyl fluorides, the B3LYP/6-311++G(d,p) calculations on the octane isomers predict that the linear isomer will be the most thermodynamically stable. In contrast, the semiempirical PM6 method, as with these other compound classes, predicts the linear isomer will be among the least thermodynamically stable.

Experimental gas phase data on the relative enthalpies of linear and branched alkanes and alcohols clearly shows that branched isomers are more thermodynamically stable than their linear counterparts. The experimental dataset for the liquid phases of these validation set compounds indicates branched alkyl compounds are more thermodynamically stable than linear analogs in the condensed state as well (Supplementary Material Table S4). For the butanols, pentanes, pentanols, hexanes, and heptanes, the liquid phase thermodynamic stability ranks within each class are exactly the same as for the gas phase, all showing that alkane linearity decreases the thermodynamic stability. For the 18 octane isomers, the liquid phase relative thermodynamic stability ranks never deviate from the gas phase ranks by more than two rank units, and the average rank difference between the gas and liquid states is negligible among these compounds (-0.06 rank units). Thus, in both the gas and liquid phases, well established
experimental data strongly indicates that branched alkylated isomers of various compound classes are always more thermodynamically stable than their linear counterparts.

A significant number of previous studies have also reported on the failure of various semiempirical, DFT, and HF ab initio methods to reproduce relative enthalpies and Gibbs free energies between linear and branched alkanes (including haloalkanes), a discrepancy commonly referred to as the branching error [67-83]. Calculations at the MPx, Gx, and CBS-x levels are typically required to achieve chemical accuracy for the relative thermodynamics of these compounds [70-72,76,77-79,81,84-86]. In addition, increasing errors in calculated $\Delta H_{f(g)}^\circ$ values with increasing alkyl chain length are known for a wide range of levels of theory (including the Gx/CBS-x levels, although such errors are typically modest [i.e., <1-2 kcal mol$^{-1}$]), but particularly for B3LYP calculations (even with large basis sets) where the $\Delta H_{f(g)}^\circ$ errors can exceed 30 kcal mol$^{-1}$ [69,78,85]. Similarly, increasing basis set size often decreases the accuracy of thermochemical calculations with many DFT methods, leading to the “getting the right answer for the wrong reason” issue, whereby more accurate results are obtained with less accurate methods [69,76-78,87].

Failure to correctly describe dispersion forces (which can be corrected using modifications to the standard model chemistries), lack of terms for describing kinetic energy density, and unoptimized relative amounts of the Becke exchange and the HF exchange (where applicable) have been put forward as the causes for some DFT models not accurately estimating alkane energies [70,72,74-76,81,82]. There is also earlier evidence for the potential problems with calculated B3LYP enthalpies and entropies for polyfluorinated compounds [76,79,88,89].
Furthermore, calculations for alkanes are commonly restricted to the global minimum, and this approach – which is common in the field – neglects thermochemical contributions from other low-energy conformers. However, such conformer distribution corrections typically correct the calculated enthalpies by <1 kcal mol$^{-1}$ [85], and not in a manner sufficient to overcome the DFT branching errors. Entropic corrections for higher energy contributing conformers are more complicated, and require an additional mixing correction [89]. As a result, the current state-of-the-art indicates well established and large errors in estimating the relative thermodynamic properties of linear and branched alkanes using most DFT methods (particularly B3LYP), necessitating either (1) the use of semiempirical methods that have been parametrized to account for these thermochemical differences, (2) the use of high-accuracy methods such as MPx, Gx, and/or CBS-x, or (3) the use of new density functionals that have, like their semiempirical counterparts, been specifically parametrized to address alkane branching errors.

Within this literature context, we then performed single point calculations at the MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels of theory on optimized B3LYP/6-311++G(d,p) geometries (i.e., MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) and B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p)) for n-PFOS/F and its monomethyl branched isomers (Table 6). This MP2 level of single point energy calculations has been previously reported to yield good accuracies of alkane branching thermochemistry [75]. For both the MP2 and B3LYP calculations, the 1-CF$_3$-PFOS and 1-CF$_3$-PFOSF are predicted to be the most thermodynamically stable isomers in this subset. However, there is a substantial destabilization of the linear n-PFOS and n-PFOSF isomers at the MP2/6-311++G(d,p) single point energy level relative to the corresponding 1-CF$_3$-PFOS/F isomer when compared to the B3LYP/6-311++G(d,p)//B3LYP/6-
311++G(d,p) data. For example, the $\Delta E_{(g)}^{\circ}$ between n-PFOS and 1-CF$_3$-PFOS increases from 4.9 kJ mol$^{-1}$ at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level to 23.3 kJ mol$^{-1}$ at the MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) level. A similar $\Delta E_{(g)}^{\circ}$ increase from 7.1 kJ mol$^{-1}$ to 25.4 kJ mol$^{-1}$ occurs between these two methods for the corresponding n-PFOSF and 1-CF$_3$-PFOSF isomers. For both compound classes, the linear isomer moves from one of the most thermodynamically stable members of each class at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) level to either the least thermodynamically stable (for n-PFOS) or second-least stable (for n-PFOSF) at the MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) level. While there are also small differences in the relative energies of the monomethyl branched PFOS/F isomers between the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) level calculations (ranging from 1 to 5 kJ mol$^{-1}$), these are small compared to the ~20 kJ mol$^{-1}$ relative destabilization of the linear isomers with the MP2 calculations. Thus, the B3LYP alkane branching effect appears to extend to the perfluoroalkanes, and is predominantly manifested as an erroneous stabilization of the linear isomers.

The M05-2X meta-hybrid density functional [19] has also been proposed to reduce the DFT branching errors, and shown to perform well on estimating the isomerization energies of a range of hydrocarbons [80,81,90]. Consequently, we also conducted M05-2X/6-311++G(d,p) level calculations on the 7 linear and monomethyl branched PFOS isomers (Table 7). With this method, we also see substantial removal of the B3LYP branching error, resulting in the linear n-PFOS becoming much less thermodynamically stable compared to the 1-CF$_3$-PFOS isomer ($\Delta G_{(g)}^{\circ}=13.5$ kJ mol$^{-1}$) versus the calculations at the B3LYP/6-311++G(d,p) level (see Table 1) which suggested that n-PFOS and 1-CF$_3$-PFOS had approximately equivalent (<2 kJ mol$^{-1}$
difference) gas phase thermodynamic stability. Thus, where higher levels of theory may be too computationally expensive for linear and branched perfluoroalkane thermochemistry studies, and in the absence of experimental data upon which to benchmark various methods, we recommend the M05-2X density functional for computational investigations of these compounds.

We also extended our studies to the linear and monomethyl branched isomers of perfluorooctanoic acid (PFOA; a well known industrial product and environmental contaminant) and the corresponding acyl fluorides (PFOAF). As with PFOS technical mixtures, the perfluoroalkyl carboxylic acids (PFCAs) such as PFOA were historically synthesized via electrochemical fluorination of linear perhydroalkane acyl fluoride precursors. As such, the perfluoroalkyl acyl fluorides are the most relevant compounds upon which to found a thermodynamic study that investigates the utility of thermochemical data for predicting the isomer distribution of technical mixtures. In contrast to the PFOS/F studies, where large method dependent thermochemical results were obtained for the linear and monomethyl branched isomers, the gas phase PM6, B3LYP/6-311++G(d,p), and MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) calculations on the PFOA/F isomers all unequivocally indicate that the linear n-PFOA/F compounds are substantially less thermodynamically stable than their 1-CF3-PFOA/F counterparts (Table 8). Therefore, the results leave no doubt as to the lack of utility of thermodynamic data for predicting the isomeric distribution of PFOA/F technical mixtures, since – as with the PFOS/F classes – the linear PFCA isomers are always the major isomers (~70%) present in the commercial products, and these compounds would need to be clearly more thermodynamically stable than any branched isomers for the approach to have either qualitative or quantitative merit. There is excellent agreement in the single point energies for the branched
PFOA/F isomers between the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) levels (1 to 3 kJ mol\(^{-1}\) differences), but – as with the PFOS/F calculations – the linear PFOA/F congener is substantially destabilized relative to 1-CF\(_3\)-PFOA/F in moving from the B3LYP to MP2 level. Thus, analogous to the perfluoroalkyl sulfonic acid/sulfonyl fluoride studies, accurate thermochemical studies of linear and branched PFCAs will necessitate calculations either at the MPx, Gx, and/or CBS-x levels, or perhaps using new density functional such as the M05-2X method discussed above. The current absence of thermochemical data on PFCAs, and perfluoroalkanes in generals, prevents an assessment of whether the M05-2X functional is a reasonable tradeoff between cost and accuracy, or whether the more expensive methods will need to be employed for accurate datasets.

As we have shown, the semiempirical PM6 method outperforms the B3LYP DFT method on a range of representative perhydroalkyl classes when compared to the experimental gas phase datasets. When this validation effort is coupled with our systematic and comprehensive gas phase investigations of both linear and branched perfluorinated and perhydrogenated alkyl sulfonic acids, as well as other selected gas and aqueous phase calculations on representative members of these classes and those of the perfluoroalkyl sulfonyl fluorides, carboxylic acids, and acyl fluorides, it appears that HF ab initio and B3LYP DFT calculations incorrectly estimate the relative thermodynamic stabilities of gas and aqueous phase linear and branched perfluoroalkyl compounds. Consequently, the semiempirical PM6 estimates for the relative thermodynamic stability of perfluoroalkylated compounds may be substantially more accurate than some ab initio or B3LYP DFT calculations, and that branched perfluoroalkyl compounds should – in the absence of experimental data refuting this well-established structure-stability trend in organic
chemistry – be considered more thermodynamically stable than their linear counterparts. Our findings also call attention for the continued requirement by research groups to first validate new ab initio and DFT computational results against both accepted qualitative and quantitative thermodynamic trends and experimental data from analogous compound classes prior to assuming the data are inherently more accurate than semiempirical calculations.

Acknowledgements

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Appendix A. Supplementary data

Standard state gas phase enthalpies for linear perfluorooctane sulfonic acid and its six monomethyl branched isomers using various semiempirical, Hartree-Fock (HF) ab initio, and B3LYP density functional theory (DFT) methods. Standard state gas phase Gibbs free energies for the C₃ through C₈ perfluoroalkyl and perhydroalkyl sulfonic acids using the semiempirical PM6 and the B3LYP/6-311++G(d,p) levels of theory. Standard state experimental liquid phase enthalpies for various linear and branched alkanes and alcohols. Supplementary data associated with this article can be found in the online version, at doi: [insert doi].
Figure Captions

**Fig. 1.** Structures of n-PFOS and its six monomethyl branched isomers. Chiral centers on the perfluoroalkyl chains are denoted by “*”.

**Fig. 2.** Calculated standard state gas phase relative Gibbs free energies ($\Delta G_{(g)}^\circ$, in kJ mol$^{-1}$) for the C$_3$ through C$_8$ perfluoroalkyl sulfonic acids using the semiempirical PM6 (MOPAC 2007 [from ref. [10]] and Gaussian 09) and the B3LYP/6-311++G(d,p) levels of theory. Gibbs free energies obtained using Gaussian 09 include the zero point energy and the thermal correction to the free energy.

**Fig. 3.** Transverse and axial views of the optimized gas phase geometries for the acid form of n-PFOS obtained at the PM6, HF/6-311++G(d,p), and B3LYP/6-311++G(d,p) levels of theory.

**Fig. 4.** Axial views of the eclipsed local minimum and helical global minimum obtained for the acid form of n-PFOS by the semiempirical PM3 method in MOPAC 2000.

**Fig. 5.** Calculated standard state gas phase relative Gibbs free energies ($\Delta G_{(g)}^\circ$, in kJ mol$^{-1}$) for the C$_3$ through C$_8$ alkyl sulfonic acids using the semiempirical PM6 and the B3LYP/6-311++G(d,p) levels of theory. Gibbs free energies include the zero point energy and the thermal correction to the free energy.
Fig. 1.
Fig. 2.
Fig. 3.
Fig. 4.

\[ \Delta H_{(g),PM_3}^0 = -25.5 \text{ kJ mol}^{-1} \]
Fig. 5.
Table 1
Calculated standard state gas phase relative Gibbs free energies ($\Delta G_{(g)}^\circ$; in kJ mol$^{-1}$) for linear perfluorooctane sulfonic acid (PFOS 89) and its six monomethyl branched isomers (PFOS 83 through 88) using various semiempirical, Hartree-Fock (HF) ab initio, and B3LYP density functional theory (DFT) methods. The relative thermodynamic stability ranking ([1]=most stable; [7]=least stable) among the 7 isomers for each computational method is given in brackets following each $\Delta G_{(g)}^\circ$ value. Absolute Gibbs free energies (in Hartrees) that include the zero point energy and the thermal correction to the free energy for the most stable isomer in each ab initio and DFT method are provided in the footnotes.

<table>
<thead>
<tr>
<th></th>
<th>PM6 MOPAC 2007$^a$</th>
<th>AM1 Gaussian 09</th>
<th>PM3 6-31G(d,p)</th>
<th>HF 6-31++G(d,p)</th>
<th>HF 6-311++G(d,p)</th>
<th>HF 6-31G(d,p)</th>
<th>HF 6-31++G(d,p)</th>
<th>HF 6-311++G(d,p)</th>
<th>B3LYP 6-31++G(d,p)</th>
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<td>1-CF$_3$-PFOS</td>
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<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>4.9 [5]</td>
<td>0.0$^b$ [1]</td>
<td>0.0$^c$ [1]</td>
<td>0.0$^d$ [1]</td>
<td>0.0$^e$ [1]</td>
<td>0.0$^f$ [1]</td>
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$^a$ from ref. [10]. $^b$ $G_{(g)}^\circ$=-2615.882713 H. $^c$ $G_{(g)}^\circ$=-2615.945487 H. $^d$ $G_{(g)}^\circ$=-2616.517885 H. $^e$ $G_{(g)}^\circ$=-2626.400439 H. $^f$ $G_{(g)}^\circ$=-2626.526222 H. $^g$ $G_{(g)}^\circ$=-2627.143643 H.
Table 2
Calculated standard state gas phase relative Gibbs free energies ($\Delta G_{(g)}^\circ$; in kJ mol$^{-1}$) for linear perfluorooctane sulfonyl fluoride (PFOSF 89) and its six monomethyl branched isomers (PFOSF 83 through 88) using various semiempirical, Hartree-Fock (HF) ab initio, and B3LYP density functional theory (DFT) methods. The relative thermodynamic stability ranking ([1]=most stable; [7]=least stable) among the 7 isomers for each computational method is given in brackets following each $\Delta G_{(g)}^\circ$ value. Absolute Gibbs free energies (in Hartrees) that include the zero point energy and the thermal correction to the free energy for the most stable isomer in each ab initio and DFT method are provided in the footnotes.

<table>
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<td>10.9</td>
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<td>3.2</td>
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<td>0.0c</td>
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$^a$ $G_{(g)}^\circ$=-2639.881198 H. $^b$ $G_{(g)}^\circ$=-2639.943426 H. $^c$ $G_{(g)}^\circ$=-2640.518843 H. $^d$ $G_{(g)}^\circ$=-2650.425499 H. $^e$ $G_{(g)}^\circ$=-2650.551556 H. $^f$ $G_{(g)}^\circ$=-2651.173272 H.
Table 3
Calculated standard state aqueous phase relative Gibbs free energies ($\Delta G_{\text{aq}}^\circ$; in kJ mol$^{-1}$) for the linear and monomethyl branched PFOS and PFOSF isomers using the PCM-PM6 and PCM-B3LYP/6-311++G(d,p) levels of theory in water. The relative thermodynamic stability ranking ([1]=most stable; [7]=least stable) among the 7 isomers for each computational method is given in brackets following each $\Delta G_{\text{aq}}^\circ$ value. The absolute Gibbs free energy (in Hartrees) that includes the zero point energy and the thermal correction to the free energy for the most stable isomer from the PCM-B3LYP/6-311++G(d,p) calculations is provided in the footnotes.

<table>
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<th>PCM-PM6$_{\text{aq}}$</th>
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<th>PCM-B3LYP/6-311++G(d,p)$_{\text{aq}}$</th>
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$^a G_{\text{aq}}^\circ$ = -2627.154633 H. $^b G_{\text{aq}}^\circ$ = -2651.179317 H.
Table 4
Calculated geometrical features for gas phase linear perfluoroctane sulfonic acid (PFOS 89) at the PM6, HF/6-311++G(d,p), and B3LYP/6-311++G(d,p) levels of theory and comparison to the reported [13,91] experimental structure of N-ethylperfluoroctane sulfonamide (N-EtPFOSA). Differences between calculated and experimental data, where available, are given in parentheses. Interatomic distances are in angstroms; bond angles are in degrees.

<table>
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<th>Interatomic distances</th>
<th>N-EtFOSA exp\textsuperscript{a}</th>
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<td>1.5732 (0.0142)</td>
<td>1.5558 (-0.0032)</td>
<td>1.5738 (0.0149)</td>
</tr>
<tr>
<td>C4-F</td>
<td>1.3363, 1.3443</td>
<td>1.3494, 1.3497</td>
<td>1.3197, 1.3204</td>
<td>1.3490, 1.3496</td>
</tr>
<tr>
<td>C5-C6</td>
<td>1.5447</td>
<td>1.5726 (0.0279)</td>
<td>1.5554 (0.0107)</td>
<td>1.5731 (0.0284)</td>
</tr>
<tr>
<td>C5-F</td>
<td>1.3320, 1.3475</td>
<td>1.3495, 1.3497</td>
<td>1.3198, 1.3207</td>
<td>1.3490, 1.3500</td>
</tr>
<tr>
<td>C6-C7</td>
<td>1.5469</td>
<td>1.5697 (0.0228)</td>
<td>1.5528 (0.0059)</td>
<td>1.5698 (0.0229)</td>
</tr>
<tr>
<td>C6-F</td>
<td>1.3345, 1.3478</td>
<td>1.3496, 1.3502</td>
<td>1.3208, 1.3209</td>
<td>1.3502, 1.3502</td>
</tr>
<tr>
<td>C7-C8</td>
<td>1.5355</td>
<td>1.5680 (0.0325)</td>
<td>1.5470 (0.0115)</td>
<td>1.5663 (0.0308)</td>
</tr>
<tr>
<td>C7-F</td>
<td>1.3359, 1.3403</td>
<td>1.3497, 1.3504</td>
<td>1.3185, 1.3218</td>
<td>1.3474, 1.3513</td>
</tr>
<tr>
<td>C8-F</td>
<td>(0.0138, 0.0101)</td>
<td>(0.0174, -0.0185)</td>
<td>(0.0115, 0.0110)</td>
<td>(0.0156, 0.0145, 0.0063)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond angles</th>
<th>H-O-S</th>
<th>n/a</th>
<th>116.7</th>
<th>112.7</th>
<th>110.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO-S=O</td>
<td>n/a</td>
<td>105.8, 108.8</td>
<td>107.5, 109.1</td>
<td>106.4, 109.3</td>
<td></td>
</tr>
<tr>
<td>O=S=O</td>
<td>n/a</td>
<td>124.5</td>
<td>123.4</td>
<td>124.3</td>
<td></td>
</tr>
<tr>
<td>O=S=O</td>
<td>n/a</td>
<td>107.9, 110.1</td>
<td>106.9, 108.4</td>
<td>107.3, 108.5</td>
<td></td>
</tr>
<tr>
<td>O-S-CH\textsubscript{3}</td>
<td>n/a</td>
<td>96.2</td>
<td>98.7</td>
<td>97.9</td>
<td></td>
</tr>
<tr>
<td>O-S-CH\textsubscript{3}</td>
<td>n/a</td>
<td>117.6 (3.7)</td>
<td>112.8 (-1.1)</td>
<td>113.3 (-0.6)</td>
<td></td>
</tr>
<tr>
<td>C7-C8-C\textsubscript{3}</td>
<td>115.2</td>
<td>116.2 (1.0)</td>
<td>113.2 (-2.0)</td>
<td>113.4 (-1.8)</td>
<td></td>
</tr>
<tr>
<td>C7-C8-F</td>
<td>108.6, 108.8</td>
<td>107.1, 107.9 (-1.5, -0.9)</td>
<td>108.3, 108.6 (-0.3, -0.2)</td>
<td>108.2, 108.2 (-0.4, -0.6)</td>
<td></td>
</tr>
<tr>
<td>C7-C8-F</td>
<td>108.1, 108.5</td>
<td>108.9, 109.4 (0.8, 0.9)</td>
<td>108.4, 108.6 (0.3, 0.1)</td>
<td>108.4, 108.4 (0.3, 0.1)</td>
<td></td>
</tr>
<tr>
<td>C7-C8-F</td>
<td>113.6</td>
<td>116.0 (2.4)</td>
<td>113.1 (-0.5)</td>
<td>113.3 (-0.3)</td>
<td></td>
</tr>
<tr>
<td>C7-C8-F</td>
<td>108.6, 108.8</td>
<td>108.9, 109.8 (0.3, 1.0)</td>
<td>108.4, 108.9 (-0.2, 0.1)</td>
<td>108.3, 108.8 (-0.3, 0.0)</td>
<td></td>
</tr>
<tr>
<td>C7-C8-F</td>
<td>114.5</td>
<td>116.0 (1.5)</td>
<td>113.1 (-1.4)</td>
<td>113.3 (-1.2)</td>
<td></td>
</tr>
<tr>
<td>C7-C8-F</td>
<td>108.0, 108.9</td>
<td>108.9, 109.9 (0.9, 1.0)</td>
<td>108.4, 108.9 (0.4, 0.0)</td>
<td>108.4, 108.8 (0.4, -0.1)</td>
<td></td>
</tr>
<tr>
<td>C7-C8-F</td>
<td>113.7</td>
<td>116.1 (2.4)</td>
<td>113.3 (-0.4)</td>
<td>113.5 (-0.2)</td>
<td></td>
</tr>
<tr>
<td>C7-C8-F</td>
<td>109.2, 109.7</td>
<td>109.1, 110.1 (-0.1, 0.4)</td>
<td>108.5, 109.1 (-0.7, -0.6)</td>
<td>108.4, 109.0 (-0.8, -0.7)</td>
<td></td>
</tr>
<tr>
<td>C7-C8-F</td>
<td>115.7</td>
<td>115.5 (-0.2)</td>
<td>114.4 (-1.3)</td>
<td>114.4 (-1.3)</td>
<td></td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th></th>
<th>C—C&lt;sub&gt;7&lt;/sub&gt;-F</th>
<th>109.0, 109.0</th>
<th>109.8, 110.6 (0.8, 1.6)</th>
<th>108.7, 109.5 (-0.3, 0.5)</th>
<th>108.8, 109.4 (-0.2, 0.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;7&lt;/sub&gt;-C&lt;sub&gt;8&lt;/sub&gt;-F</td>
<td>110.0, 110.7, 110.9</td>
<td>113.2, 113.8, 114.0</td>
<td>108.5, 110.6, 111.0</td>
<td>(-1.5, -0.1, 0.1)</td>
<td>108.7, 110.6, 111.0</td>
</tr>
</tbody>
</table>

<sup>a</sup> from ref. [13].<sup>b</sup> n/a=not available.
Table 5
Comparison between experimental, PM6, and B3LYP/6-311++G(d,p) gas phase standard state relative enthalpies ($\Delta H^{\circ}_g$) for various parent and substituted linear and branched alkanes. The relative enthalpic rank order within each set of compounds is given in brackets. For each group of compounds, the root mean squared error (RMSE) for both the $\Delta H^{\circ}_g$ and rank order (in brackets) is provided. Calculated relative gas phase standard state relative Gibbs free energies ($\Delta G^{\circ}_g$) and associated rank orders are also given. Both calculated $\Delta H^{\circ}_g$ and $\Delta G^{\circ}_g$ values include zero point energy and thermal corrections.

<table>
<thead>
<tr>
<th>Compound</th>
<th>expt$^{a}$ $\Delta H^{\circ}_g$ (kJ mol$^{-1}$)</th>
<th>PM6 $\Delta H^{\circ}_g$ (kJ mol$^{-1}$)</th>
<th>B3LYP/6-311++G(d,p) $\Delta H^{\circ}_g$ (kJ mol$^{-1}$)</th>
<th>expt$^{a}$ $\Delta G^{\circ}_g$ (kJ mol$^{-1}$)</th>
<th>PM6 $\Delta G^{\circ}_g$ (kJ mol$^{-1}$)</th>
<th>B3LYP/6-311++G(d,p) $\Delta G^{\circ}_g$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-methyl-2-propanol</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>RMSE 5.3 [0.0]</td>
</tr>
<tr>
<td>2-methyl-2-butanol</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>RMSE 2.5 [0.0]</td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>0.9 [3]</td>
<td>5.5 [3]</td>
<td>RMSE 2.5 [0.0]</td>
</tr>
<tr>
<td>Heptane</td>
<td>18.1 [9]</td>
<td>14.5 [8]</td>
<td>11.3 [7]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>RMSE 2.5 [0.0]</td>
</tr>
<tr>
<td>2,2-dimethylpentane</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>1.4 [3]</td>
<td>5.3 [3]</td>
<td>RMSE 2.5 [0.0]</td>
</tr>
<tr>
<td>Octane</td>
<td>17.5 [18]</td>
<td>17.1 [13]</td>
<td>11.4 [10]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>RMSE 3.0 [0.9]</td>
</tr>
<tr>
<td>Compound</td>
<td>Value 1 [Ref]</td>
<td>Value 2 [Ref]</td>
<td>Value 3 [Ref]</td>
<td>Value 4 [Ref]</td>
<td>Value 5 [Ref]</td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>---------------</td>
<td>---------------</td>
<td>---------------</td>
<td>---------------</td>
<td>---------------</td>
<td></td>
</tr>
<tr>
<td>2,2,3,3-tetramethylbutane</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>7.5 [6]</td>
<td>24.6 [15]</td>
<td>35.4 [16]</td>
<td></td>
</tr>
</tbody>
</table>

RMSE: 6.0 [3.3]  RMSE: 12.2 [7.4]

* from ref. [92].
Table 6
Calculated standard state gas phase relative single point energies ($\Delta E(g)°$; in kJ mol$^{-1}$) for the linear and monomethyl branched PFOS and PFOSF isomers at the B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) levels of theory. The relative thermodynamic stability ranking ([1]=most stable; [7]=least stable) among the 7 isomers for each computational method is given in brackets following each $\Delta E(g)°$ value. The absolute single point energy (in Hartrees) for the most stable isomer in each method are provided in the footnotes.

<table>
<thead>
<tr>
<th>PFOS</th>
<th>B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p)</th>
<th>MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-CF$_3$-PFOS/F</td>
<td>83 [1]</td>
<td>0.0$^a$ [1]</td>
</tr>
<tr>
<td>4-CF$_3$-PFOS/F</td>
<td>86 [6]</td>
<td>15.4 [6]</td>
</tr>
</tbody>
</table>

$^a$ $E(g)°$=-2627.206756 H. $^b$ $E(g)°$=-2621.930757 H. $^c$ $E(g)°$=-2651.224588 H. $^d$ $E(g)°$=-2645.923995 H.
Table 7
Calculated standard state gas phase relative enthalpies ($\Delta H(g)^\circ$, in kJ mol$^{-1}$), Gibbs free energies ($\Delta G(g)^\circ$, in kJ mol$^{-1}$), and single point energies ($\Delta E(g)^\circ$, in kJ mol$^{-1}$) for the linear and monomethyl branched PFOS isomers at the M05-2X/6-311++G(d,p) level of theory. The relative thermodynamic stability ranking ([1]=most stable; [7]=least stable) among the 7 isomers for each computational method is given in brackets following each $\Delta H(g)^\circ/\Delta G(g)^\circ/\Delta E(g)^\circ$ value. The absolute enthalpies and energies (in Hartrees) for the most stable isomer in each column are provided in the footnotes.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>$\Delta H(g)^\circ$</th>
<th>$\Delta G(g)^\circ$</th>
<th>$\Delta E(g)^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-CF$_3$-PFOS</td>
<td>83</td>
<td>0.0$^a$ [1]</td>
<td>0.0$^b$ [1]</td>
</tr>
</tbody>
</table>

$^a$ $H(g)^\circ$=-2626.885146 H. $^b$ $G(g)^\circ$=-2626.969258 H. $^c$ $E(g)^\circ$=-2627.041197 H.
Table 8
Calculated standard state gas phase relative enthalpies ($\Delta H(g)^\circ$; in kJ mol$^{-1}$), Gibbs free energies ($\Delta G(g)^\circ$; in kJ mol$^{-1}$), and single point energies ($\Delta E(g)^\circ$; in kJ mol$^{-1}$) for the linear and monomethyl branched PFOA and PFOAF isomers at the PM6, B3LYP/6-311++G(d,p), B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p), and MP2/6-311++G(d,p)//B3LYP/6-311++G(d,p) levels of theory. The relative thermodynamic stability ranking ([1]=most stable; [7]=least stable) among the 6 isomers for each computational method is given in brackets following each $\Delta H(g)^\circ$/ $\Delta G(g)^\circ$/ $\Delta E(g)^\circ$ value. The absolute enthalpies and energies (in Hartrees) for the most stable isomer in each ab initio and DFT method are provided in the footnotes.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>PM6 $\Delta H(g)^\circ$</th>
<th>PM6 $\Delta G(g)^\circ$</th>
<th>PM6 $\Delta E(g)^\circ$</th>
<th>PM6 $\Delta H(g)^\circ$</th>
<th>PM6 $\Delta G(g)^\circ$</th>
<th>PM6 $\Delta E(g)^\circ$</th>
<th>PM6 $\Delta H(g)^\circ$</th>
<th>PM6 $\Delta G(g)^\circ$</th>
<th>PM6 $\Delta E(g)^\circ$</th>
<th>PM6 $\Delta H(g)^\circ$</th>
<th>PM6 $\Delta G(g)^\circ$</th>
<th>PM6 $\Delta E(g)^\circ$</th>
<th>PM6 $\Delta H(g)^\circ$</th>
<th>PM6 $\Delta G(g)^\circ$</th>
<th>PM6 $\Delta E(g)^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-CF$_3$-PFOA/F</td>
<td>83</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>0.0$^a$ [1]</td>
<td>0.0$^b$ [1]</td>
<td>0.0$^c$ [1]</td>
<td>0.0$^d$ [1]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>0.0$^e$ [1]</td>
<td>0.0$^f$ [1]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
</tr>
</tbody>
</table>

$^a$ $H(g)^\circ$=-1953.969844 H. $^b$ $G(g)^\circ$=-1954.048358 H. $^c$ $E(g)^\circ$=-1949.104917 H. $^d$ $E(g)^\circ$=-1949.932014 H. $^e$ $H(g)^\circ$=-1977.991802 H. $^f$ $G(g)^\circ$=-1978.070375 H. $^g$ $E(g)^\circ$=-1978.113888 H. $^h$ $E(g)^\circ$=-1973.917275 H.
References


[34] C. Moller, M.S. Plesset, Phys. Rev. 46 (1934) 618.


Supplementary Material for:

Comparative semiempirical, ab initio, and density functional theory study on the thermodynamic properties of linear and branched perfluoroalkyl sulfonic acids/sulfonyl fluorides, perfluoroalkyl carboxylic acid/acyl fluorides, and perhydroalkyl sulfonic acids, alkanes, and alcohols

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### Table S1

Calculated standard state gas phase relative enthalpies ($\Delta H^\circ_{(g)}$; in kJ mol$^{-1}$) for linear perfluorooctane sulfonic acid (PFOS 89) and its six monomethyl branched isomers (PFOS 83 through 88) using various semiempirical, Hartree-Fock (HF) ab initio, and B3LYP density functional theory (DFT) methods. The relative thermodynamic stability ranking ([1]=most stable; [7]=least stable) among the 7 isomers for each computational method is given in brackets following each $\Delta H^\circ_{(g)}$ value. Absolute enthalpies (in Hartrees) that include the zero point energy and the thermal correction to the enthalpy for the most stable isomer in each ab initio and DFT method are provided in the footnotes.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>MOPAC 2007$^a$</th>
<th>Gaussian 09</th>
<th>AM1</th>
<th>PM3</th>
<th>6-31G(d,p)</th>
<th>6-31++G(d,p)</th>
<th>HF</th>
<th>6-311++G(d,p)</th>
<th>6-31G(d,p)</th>
<th>6-31++G(d,p)</th>
<th>B3LYP</th>
<th>6-311++G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-CF$_3$-PFOS</td>
<td>83</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>0.0 [1]</td>
<td>4.2 [4]</td>
<td>0.0$^b$ [1]</td>
<td>0.0$^b$ [1]</td>
<td>0.0$^b$ [1]</td>
<td>0.0$^b$ [1]</td>
<td>0.0$^b$ [1]</td>
<td>0.0$^b$ [1]</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ from ref. [1]. $^b$ $H^\circ_{(g)}$=-2615.800350 H. $^c$ $H^\circ_{(g)}$=-2615.862566 H. $^d$ $H^\circ_{(g)}$=-2616.435292 H. $^e$ $H^\circ_{(g)}$=-2626.313167 H. $^f$ $H^\circ_{(g)}$=-2626.438060 H. $^g$ $H^\circ_{(g)}$=-2627.055825 H.
**Table S2**

Calculated standard state gas phase relative Gibbs free energies ($\Delta G^{\circ}_w$; in kJ mol$^{-1}$) for the C$_3$ through C$_7$ perfluoroalkyl sulfonic acids using the semiempirical PM6 and the B3LYP/6-311+G(d,p) levels of theory. Gibbs free energies include the zero point energy and the thermal correction to the free energy. Absolute Gibbs free energies for the B3LYP/6-311+G(d,p) calculations are also provided.

<table>
<thead>
<tr>
<th>HG Substitution</th>
<th>Congener #</th>
<th>PM6-Gaussian 09</th>
<th>B3LYP/6-311+G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\Delta G^{\circ}_w$</td>
<td>Stability rank</td>
</tr>
<tr>
<td>C$_3$ n-propyl</td>
<td>1</td>
<td>26.8</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0</td>
<td>1</td>
</tr>
<tr>
<td>C$_4$ 1,1'-dimethylethyl</td>
<td>1</td>
<td>0.0</td>
<td>1</td>
</tr>
<tr>
<td>1-methylpropyl</td>
<td>2</td>
<td>57.5</td>
<td>2</td>
</tr>
<tr>
<td>2-methylpropyl</td>
<td>3</td>
<td>62.6</td>
<td>3</td>
</tr>
<tr>
<td>n-butyl</td>
<td>4</td>
<td>77.7</td>
<td>4</td>
</tr>
<tr>
<td>C$_5$ 1-ethylpropyl</td>
<td>1</td>
<td>56.3</td>
<td>6</td>
</tr>
<tr>
<td>1,1'-dimethylpropyl</td>
<td>2</td>
<td>0.0</td>
<td>1</td>
</tr>
<tr>
<td>1,2-dimethylpropyl</td>
<td>3</td>
<td>38.3</td>
<td>3</td>
</tr>
<tr>
<td>2,2'-dimethylpropyl</td>
<td>4</td>
<td>15.3</td>
<td>2</td>
</tr>
<tr>
<td>1-methylbutyl</td>
<td>5</td>
<td>43.3</td>
<td>4</td>
</tr>
<tr>
<td>2-methylbutyl</td>
<td>6</td>
<td>59.6</td>
<td>7</td>
</tr>
<tr>
<td>3-methylbutyl</td>
<td>7</td>
<td>49.8</td>
<td>5</td>
</tr>
<tr>
<td>n-pentyl</td>
<td>8</td>
<td>61.2</td>
<td>8</td>
</tr>
<tr>
<td>C$_6$ 1-ethyl-1'-methylpropyl</td>
<td>1</td>
<td>23.4</td>
<td>5</td>
</tr>
<tr>
<td>1-ethyl-2-methylpropyl</td>
<td>2</td>
<td>59.9</td>
<td>14</td>
</tr>
<tr>
<td>1,1',2-trimethylpropyl</td>
<td>3</td>
<td>4.1</td>
<td>2</td>
</tr>
<tr>
<td>1,2,2'-trimethylpropyl</td>
<td>4</td>
<td>17.8</td>
<td>3</td>
</tr>
<tr>
<td>2,2'-dimethylpropyl</td>
<td>5</td>
<td>62.6</td>
<td>4</td>
</tr>
<tr>
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Table S3
Calculated standard state gas phase relative Gibbs free energies (ΔG°(g); in kJ mol⁻¹) for the C₃ through C₇ alkyl sulfonic acids using the semiempirical PM6 and the B3LYP/6-311++G(d,p) levels of theory. Gibbs free energies include the zero point energy and the thermal correction to the free energy. Absolute Gibbs free energies for the B3LYP/6-311++G(d,p) calculations are also provided.

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**Table S4**

Comparison between experimental liquid phase standard state relative enthalpies (Δ\(H_\circ\)) for various parent and substituted linear and branched alkanes. The relative enthalpic rank order within each set of compounds is given in brackets.

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\(^a\) from ref. [2]. \(^b\) crystalline data as this compound is a solid at 25°C.
References