Theoretical Studies of the Conformations and ^{19}F NMR Spectra of Perfluorooctanesulfonates (PFOS) and Perfluorooctanesulfonamides (PFOSamides)

Liu P[a], Goddard JD[a], Arsenault G[b,*], Gu J[c], McAlees A[b], McCrindle R[a] and Robertson V[c].
[a] Chemistry Dept., University of Guelph, Guelph, Ontario, N1G 2W1, Canada
[b] Wellington Laboratories Inc., Research Division, Guelph, Ontario, Ontario, N1G 3M5, Canada
[c] NMR Center, University of Guelph, Guelph, Ontario, N1G 2W1, Canada

* corresponding author. Tel.: +1 519 822 2436; fax: +1 519 822 2849
E-mail address: gilles@well-labs.com (G.Arsenault)

Introduction

Perfluorooctanesulfonate (PFOS) derivatives have been used in a variety of industrial, commercial and consumer products. Recently, they have been the subject of interest because of their presence as global pollutants[1-3] and potential toxicity. [4-5] The production of PFOS from linear alkyl precursors using electrochemical fluorination is not a clean process, but instead generates complex mixtures. Commercial PFOS is largely a mixture of ca. 65% linear and ca. 35% branched isomers[6]. Recently, isolation of the main isomers has allowed the characterization of 11 of them and their quantification in technical PFOS by ^{19}F NMR spectroscopy[7]. The branched isomers containing a chiral carbon exhibit AB patterns for most of the CF_2 moieties present in the perfluoroalkyl chain. This information may help provide insight into the conformations of perfluoroalkyl chains in solution.

The objective of this work was to determine the best computational method to model the preferred conformations of PFOS derivatives, the energy differences between them and if these results can be used to explain the temperature dependence of their NMR spectra.

Experimental

Computational Modeling: Predictions of the optimized geometries and of the chemical shifts and coupling constants were carried out with the Gaussian03 program suite.[8] Theoretical models examined were HF (Hartree-Fock), four density functional schemes: B3LYP, PBE1PBE, B3P86, B3PW91, and second order Moller-Plesset perturbation theory, MP2. Six basis sets were used for geometry optimizations and NMR calculations on a set of smaller organofluorine compounds in method evaluations: 6-31G(d,p), 6-31++G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311G(2d,2p), and 6-311++G(2d,2p).

NMR Experiments: ^{19}F spectra were recorded at 375.50 MHz on a Bruker Avance DPX 400 NMR spectrometer equipped with a Bruker SEF $^{19}F/^{1}H$ dual probehead. The scans were obtained in 64K data points over a 56.497 kHz spectral width (0.580 s acquisition time) using a 30° flip-angle pulse with ^{1}H decoupling. The ^{19}F 90° pulse width was 8.0 μs. 10 s for the linear and 2 s for the branched relaxation delays was employed. The free induction decays (FIDs) were processed using exponential multiplication (line-broadening 2 Hz) before Fourier transformation.

Results and Discussion

Theoretical models examined were HF (Hartree Fock), B3LYP, PBE1PBE, B3P86, B3PW91, MP2. The basis sets for geometry optimizations and NMR calculations were 6-31G(d,p), 6-31++G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311G(2d,2p), and 6-311++G(2d,2p). Four molecules (CF3-SO2OH; CF3-COOH; C2F6; C3F8) containing 5 different fluorines were examined to test the various models. Adding diffuse functions improves the performance of most methods except for Hartree Focks (HF). The statistics on predictions of the ^{19}F NMR chemical shifts indicated that the MP2 model gives good results for most basis sets, but the MP2-GIAO calculations were very time consuming and therefore, realistically, could not be used for calculations of large molecules such as PFOS. However, two more efficient methods were found to give satisfactory NMR shift predictions and therefore were evaluated for the PFOS systems: 1) PBE1PBE-GIAO/6-311++G(2d,2p)//PBE1PBE/6-31G(d,p) and 2) B3LYP-GIAO/6-31++G(d,p)//B3LYP/6-31G(d,p)[8]. The former method gave mean absolute deviation (MAD) values > 5ppm. The latter method gave the following MAD values for PFOSA: CF_2 - 1.8 ppm; terminal CF_3 – 2.2 ppm; branch CF_3 – 1.6 ppm; CF – 3.8 ppm. Therefore, the latter method was used for further calculations in this study. As with other previous studies[9,10], the model predicts the perfluoroalkyl chain to adopt the helical conformation.

The ^{19}F NMR spectra (CF_2 region) of N-benzyl PFOSulfonamide and the 5-trifluoromethyl branched isomer are shown in figure 1. The 7 CF_2 moieties in the straight chain isomer appear as broad singlets at ambient temperature. For the 5-trifluoromethyl branched isomer, all the CF_2s appear as AB quartets due to the chirality at carbon-5. Calculations show that the highest internal rotational energy barriers about C_5-C_6 for linear and branched PFOS are *ca*. 6 to 7 kcal/mol. The branch CF_3 stabilizes slightly the *gauche* conformer when compared to the linear PFOS. The two lowest energy conformers found, having similar energies, were the *anti* (*a*-) (*D*C4C5C6C7 = -137.3) and the "twisted" *gauche* (*g*-) (*D*C4C5C6C7 = -46.3). Both conformers would be expected to contribute to the observed chemical shifts and spin-spin couplings. The anti- and *g*- conformer of the C5-branched PFOSamide are shown in figure 2. A large $^5J_{FF}$ coupling of 6.8 Hz has been measured between the fluorines on C-7 and the fluorines on C-4 and C-8 supporting the close proximity of these fluorine atoms.

Variable temperature ^{19}F NMR experiments were performed on both N-benzyl PFOSulfonamide and its 5-trifluoromethyl branched isomer. Between 45 ºC and -50 ºC, the CF_2 signals in the ^{19}F NMR spectra of the branched PFOSamide appear as distinct AB quartets. At -70 ºC, splittings of the C-1 signals for both linear and branched isomers were observed. The C-1 signal for linear PFOSamide (a) appears as an AB quartet (see figure 3), and the C-1 signal for branched PFOSamide (b) appears as two AB quartets (see figure 4). The variable temperature NMR spectra suggests a slow exchange near the C-1 carbon at low temperatures. Relaxed potential energy scans calculations located two minima when rotating about the S-N bond of the linear PFOSamide. Conformer A is 0.18 kcal/mol more stable and the barrier for the transformation between the two conformers is 4.1 kcal/mol (see figures 5 & 6). The observed further splittings in the NMR spectra at the lowest temperatures are due to the presence of two chains locked with different conformations of the end groups.

Conclusions

1. Good predictions of the 19F chemical shifts were obtained for the PFOS molecules with a computationally approach [B3LYP GIAO 6-31++G(d,p)//B3LYP 6-31G(d,p)] that is relatively in expensive.
2. The g conformer of the C-5 branched compound shows large $^5J_{FF}$ couplings for the terminal CF_3 that are rationalized on the basis of the F—F distances in the optimized structure.
3. At low temperatures, the splitting observed in the NMR spectrum at C-1 can be explained by the existence of the two conformers predicted in this study.

Further work is required to explain how the influence of the chirality at C-5 in the branched isomer is transferred along the perfluoroalkyl chain all the way to the geminal fluorines on C-1[7].

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Figure 1. ^{19}F NMR spectra (CF_2 region) at ambient temperature for the linear and the C_5-branched isomer

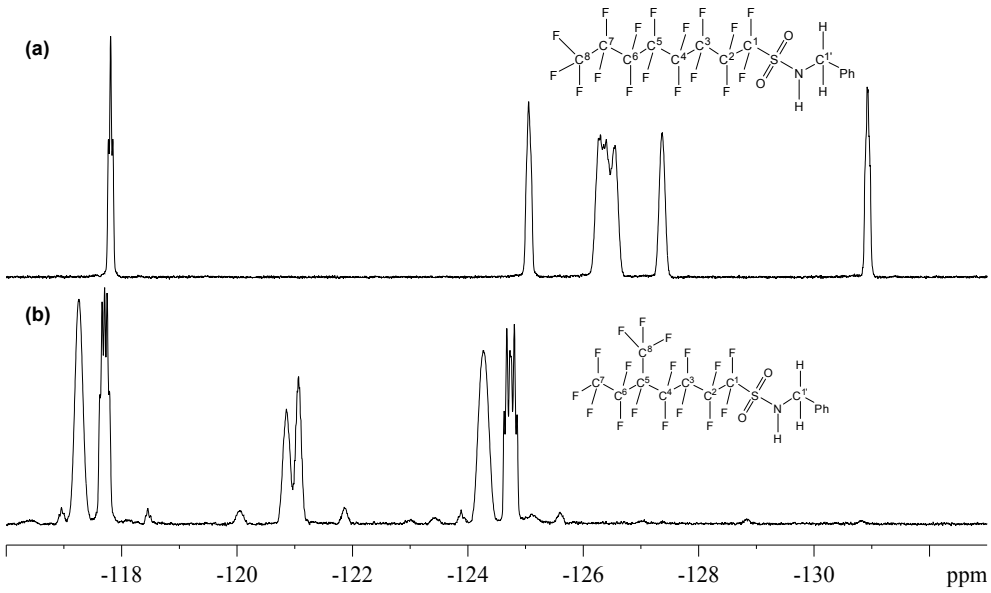
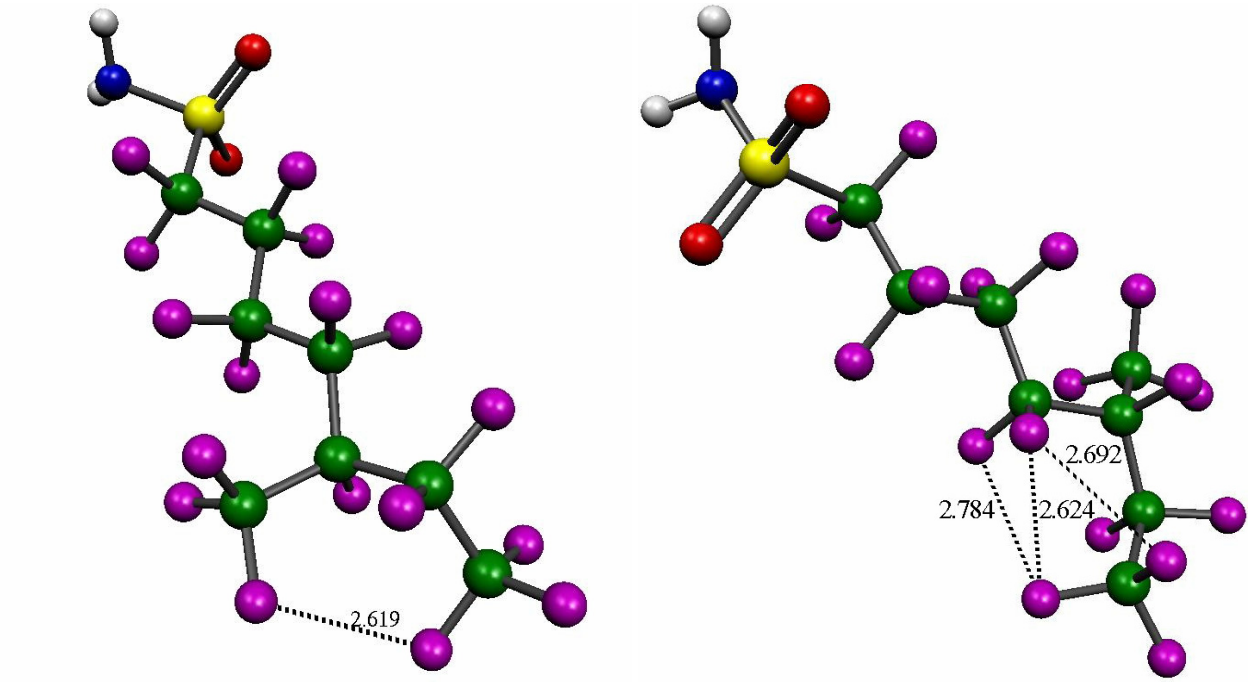


Figure 2. Calculated proximity of the terminal and branched CF_3 groups for the *anti*- and *gauche* conformers of the C_5-branched isomer



***anti*-conformer** ***gauche*-conformer**

Figure 3. ^{19}F NMR CF_2 signal at C-1 for the linear isomer

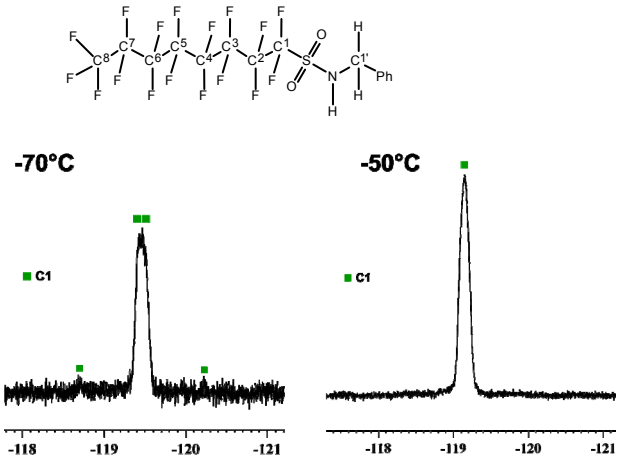


Figure 4. ^{19}F NMR CF_2 signal at C-1 for the branched isomer

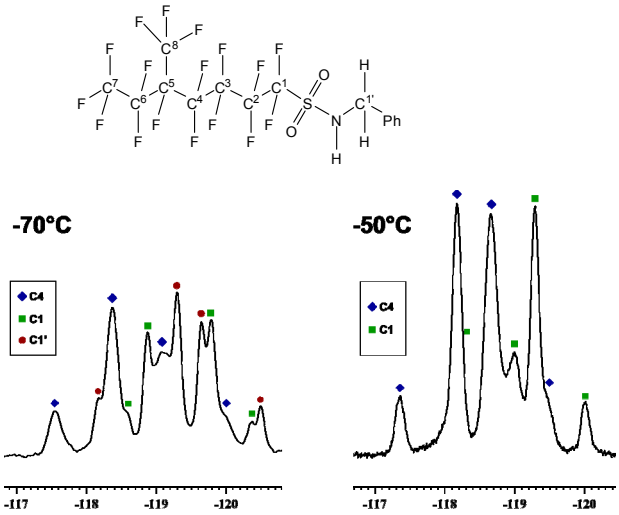
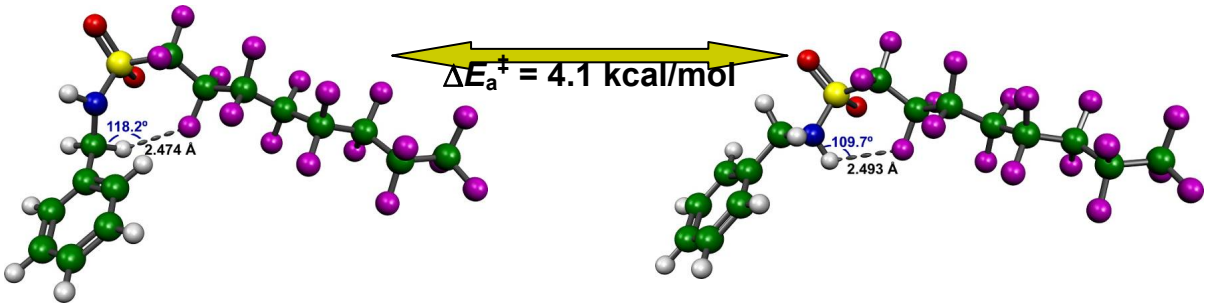


Figure 5. Two conformers from restricted rotation about the S-N bond



*The C–F … H–C interaction in conformer **A** of the linear PFOSamide. Torsion angle $\phi(C_1\text{-}S\text{-}N\text{-}C_{1'}) = 71.0°$*

*The C–F … H–N interaction in conformer **B** of the linear PFOSamide. Torsion angle $\phi(C_1\text{-}S\text{-}N\text{-}C_{1'}) = -105.1°$*

Figure 6. Relative energies between the two conformers from restricted rotation about the S-N bond