

# Structural and electronic properties of PFOS and LiPFOS

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## Abstract

The structural and electronic properties of perfluorinated surfactants perfluorooctane sulfonate (PFOS) and lithium perfluorooctane sulfonate (LiPFOS) have been investigated theoretically by performing semi-empirical molecular orbital theory at the level of AM1 calculations. The optimized structure and the electronic properties of the molecules are obtained. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* PFOS; LiPFOS; AM1 method

## 1. Introduction

Perfluorinated surfactants perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are chemicals used to produce a range of products from fire fighting foams, coatings for fabrics, leather, and some paper products, to industrial uses such as mist suppressants in acid baths. On 16 May 2000, following negotiations between EPA and 3M, the only US manufacturer of PFOS, the company announced that it will voluntarily phase out and find substitutes for PFOS [1]. Lithium perfluorooctane sulfonate (LiPFOS) is presently registered with the EPA as insecticide for use in the formulation of wasp/hornet bait stations [2]. 3M products including some of their Scotchgard lines were reported to phase out by the end of 2000 based on data submitted to EPA. Data indicated that the PFOS chemicals are very persistent in the environment, have strong tendency to accumulate

in human and animal tissues, and could potentially pose a risk to human health and the environment [3–6].

Fluorinated organic compounds (FOCs) group which PFOS belongs have raised much concern than their polychlorinated organic compounds (POCs) which include the environmentally persistent polychlorinated biphenyls (PCBs). Results of the works by Giesy and Kannan [7] and Hansen et al. [8] showed that PFOS is globally distributed with concentrations in remote areas as well as urban areas and in addition to being persistent, PFOS is bioaccumulative and is distributed in remote marine environments including polar regions. Olsen et al. [9] measured mean serum PFOS levels of 3M Company's fluorochemical production workers and reported no substantial changes in serum hepatic enzymes, cholesterol, or lipoproteins associated with PFOS less than 6 ppm. However, subchronic studies in rats and primates indicate a potential for cumulative toxicity with PFOS with the primary effect related to metabolic wasting with hypolipidemia as a consistent finding [9].

Little is known of the potential for biodegradation

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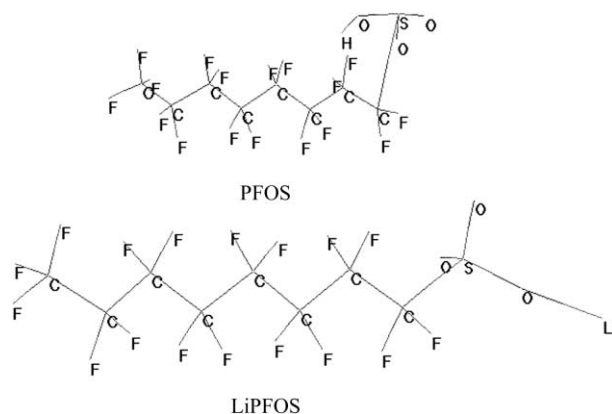


Fig. 1. The optimized structures of PFOS,  $C_8F_{17}SO_3H$ , and LiPFOS,  $C_8F_{17}SO_3Li$ .

of fluorinated sulfonates. *Pseudomonas* sp., strain D2 completely defluorinated difluoromethane sulfonate (DFMS); defluorinated only those compounds containing hydrogen (2,2,2-trifluoroethane sulfonate (TES) and 1H,1H,2H,2H-perfluorooctane sulfonate (H-PFOS)). However, trifluoromethane sulfonate (TFMS) and PFOS were not degraded [10].

Zhang and Lerner [11] recently investigated the structural properties of PFOS anion and its graphite intercalation compounds both theoretically and experimentally. In this study, we have investigated the structural and electronic properties of PFOS and LiPFOS theoretically by performing semi-empirical molecular orbital calculations, because of their biological and environmental importance.

## 2. Method of calculation

In the present study, PFOS and LiPFOS have been considered theoretically by performing the Austin Model 1 (AM1) type semi-empirical molecular orbital (MO) calculations. The AM1 semi-empirical method [12] within the unrestricted Hartree–Fock (UHF) [13] formalisms is sufficient to study the systems considered in this work.

Geometry optimization is carried out by using a conjugate gradient method (Polak–Ribiere algorithm [14]), then the electronic structure of the PFOS and LiPFOS systems are calculated by applying the semi-empirical molecular orbital AM1 method within the UHF level. The SCF convergency is set to 0.001 kcal/

mol in the calculations. We have performed all the calculations by using the HyperChem-5.1 packet.

In the calculations UHF formalism is applied for PFOS and LiPFOS systems with triplet symmetry. The closed formula for PFOS and LiPFOS are in the form  $C_8F_{17}SO_3H$  and  $C_8F_{17}SO_3Li$ , respectively. The optimized structures with atomic labels are shown in Fig. 1.

## 3. Results and discussion

Some molecular information about the systems considered are given in Table 1. The AM1 geometry optimization yields a helical structure as the stable form of PFOS and almost linear structure as the stable form of LiPFOS. The front and side views of the optimized geometries of PFOS and LiPFOS are shown in Fig. 2. Carbon–carbon distances in PFOS vary starting from the free-end going toward the sulfur-end, are 1.617, 1.608, 1.612, 1.612, 1.609, 1.627, 1.529 Å. The same quantities in LiPFOS take

Table 1  
Some molecular information about PFOS and LiPFOS systems

Quantity	PFOS	LiPFOS
# of electrons	176	176
# of occupied $e^-$ s ( $\alpha$ )	89	89
# of occupied $e^-$ s ( $\beta$ )	87	87
# of total orbitals	117	120
Ground state multiplicity	Triplet	Triplet
Molecular point group	$C_1$	$C_1$

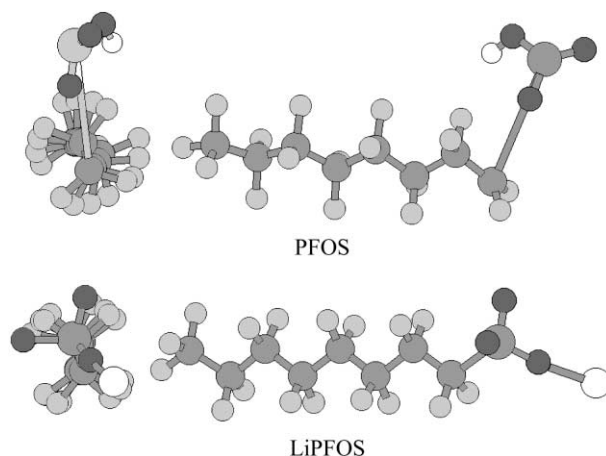


Fig. 2. The front and side views helical PFOS and almost linear LiPFOS.

the values of 1.617, 1.609, 1.612, 1.612, 1.612, 1.616, 1.586 Å, respectively. Substitution of hydrogen or lithium makes a considerable change in the structure; hydrogen atom bonded to one of the oxygen atoms aligns toward the body of the system, however lithium atom makes a tail-like bonding away from the body of the system. On the other hand, the orientation of oxygen atoms are also considerably different in both systems. The most striking point is that the carbon–sulfur distance is quite large (4.463 Å) in PFOS, and it is in a moderate range (2.080 Å) in LiPFOS. Oxygen–sulfur distances are different in both systems; in PFOS

sulfur–oxygen (with hydrogen) distance is 1.651 Å, and in LiPFOS sulfur–oxygen (with lithium) distance is 1.486 Å. Carbon–fluorine distances vary in the range of 1.322–1.369 Å in PFOS and 1.364–1.372 Å in LiPFOS.

The calculated excess charge on the atoms are given in Fig. 3. In PFOS, carbon atoms have positive excess charge, their magnitude vary from +0.094 to +0.396 electron charge; fluorine atoms have negative excess charge, their magnitude vary from –0.053 to –0.131 electron charge. A positive charge accumulation of magnitude 2.164 units takes place on sulfur

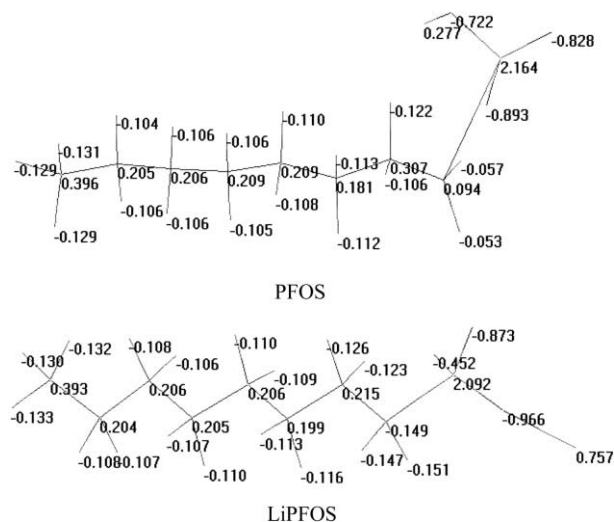


Fig. 3. Excess charge (in units of electron charge) on the atoms of PFOS and LiPFOS.

Table 2  
Energy values (in kcal/mol) of PFOS and LiPFOS systems

Quantity	PFOS	LiPFOS
Total energy	– 240791.48	– 240590.37
Binding energy	– 2873.38	– 2816.81
Isolated atomic energy	– 237918.10	– 237773.55
Electronic energy	– 1412403.37	– 1425149.90
Core–core interaction	1171611.90	1184559.54
Heat of formation	– 887.95	– 845.08

and negative charge accumulation takes place on oxygen atoms with magnitudes of  $-0.722$ ,  $-0.828$ ,  $-0.893$  units. Hydrogen atom has  $+0.277$  unit of excess charge. On the other hand, in LiPFOS the carbon atom bonded to sulfur has  $-0.149$  unit excess charge, rest of the carbon atoms have positive excess charge varying from  $+0.199$  to  $+0.393$  unit charge; fluorine atoms have negative excess charges varying from  $-0.106$  to  $-0.151$  unit. Sulfur atom has  $+2.092$  units of charge, while oxygen atoms have  $-0.452$ ,  $-0.873$ ,  $-0.966$  unit charge, lithium atom has a positive excess charge of  $+0.757$  unit of electron charge.

Calculated energies are given in Table 2. PFOS has relatively larger binding energy than LiPFOS; the magnitudes of binding energies are about  $-2873$  and  $-2817$  kcal/mol, respectively. On the other hand, the heat of formation of the systems studied are exothermic, PFOS has larger heat of formation ( $-888$  kcal/mol) than LiPFOS ( $-845$  kcal/mol). According to the energetics of the systems studied PFOS is relatively more stable than LiPFOS explaining its' persistence in the environment and resistance to defluorination by bacteria.

Table 3

HOMO, LUMO, the interfrontier molecular orbital energy gap,  $\Delta E$ , and the molecular orbital energies of the lowest and the highest levels (in eV) of PFOS and LiPFOS systems. The dipole moments,  $\mu$ , are in Debyes

Quantity	Orbital	PFOS	LiPFOS
HOMO	$\alpha$	– 10.379	– 9.071
	$\beta$	– 12.264	– 9.912
LUMO	$\alpha$	– 1.254	– 0.746
	$\beta$	– 1.367	– 1.426
$\Delta E$	$\alpha$	9.125	8.325
	$\beta$	10.897	8.486
Lowest level	$\alpha$	– 53.397	– 53.010
	$\beta$	– 53.396	– 53.010
Highest level	$\alpha$	5.013	4.129
	$\beta$	5.215	4.595
$\mu_x$		– 1.254	– 0.943
$\mu_y$		1.647	– 13.155
$\mu_z$		– 1.223	3.041
$\mu$		2.404	13.535

The molecular orbital energy (eigenvalue) spectrum of the systems studied are shown in Fig. 4. The highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO, respectively) energies and the interfrontier molecular orbital energy gap (LUMO–HOMO energy difference,  $\Delta E$ ) with the lowest and highest level energy values are given in Table 3. The LUMO–HOMO gap of PFOS (9.125 eV) is relatively larger than that of LiPFOS (8.325 eV) for  $\alpha$  orbitals, however the same quantities for  $\beta$  orbitals are 10.897 and 8.486 eV, respectively. It is interesting to note that the gap of LiPFOS for  $\alpha$  and

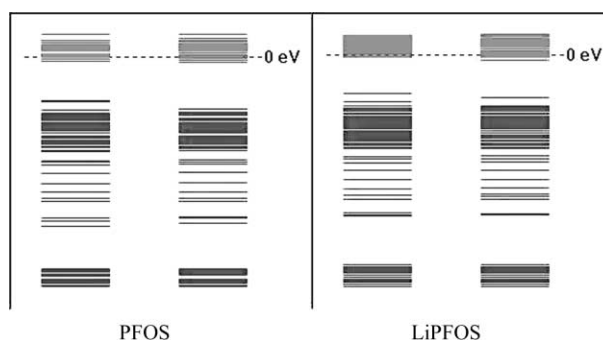


Fig. 4. The molecular orbital energy spectrum of PFOS and LiPFOS. The left and the right columns are for the  $\alpha$  and the  $\beta$  orbitals, respectively.

$\beta$  orbitals are close to each other, however the difference in the gap of  $\alpha$  and  $\beta$  orbitals in PFOS is about 1.722 eV. The absorption properties of PFOS and LiPFOS are expected to be different and needs experimental elucidation.

The calculated dipole moment values of the systems considered are also given in Table 3. PFOS has relatively small dipole moment with respect to the dipole moment of LiPFOS. LiPFOS molecule with larger dipole moment might be more polar in solutions and may therefore be more vulnerable to degradative attack.

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