

Theoretical Study of the Chemical Stability of Isomers Of Linear Alkylbenzenesulfonates

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ABSTRACT: Two homologues of linear alkylbenzenesulfonates (LAS), widely used for their surfactant properties in the formulation of detergents and cosmetics, are the subject of this work. For each of the isomers of these two homologues, global parameters of chemical stability and reactivity such as the energy gap, the chemical potential, the hardness and the nucleophile index were calculated with the density functional method B3LYP / 6-311G (d, p) (solvent: water, IEFPCM method). It emerges from this study that the benzene ring on the second carbon of the linear chain confers on these isomers a greater stability compared to the others. Similarly, stability is enhanced by the meta position of the sulfonate substituent on the benzene ring, relative to the para position.

KEY WORDS: Linear alkylbenzenesulfonates, DFT method, chemical stability, influence, substituent position.

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I INTRODUCTION

Linear alkylbenzenesulfonates (LAS) are compounds comprising a linear alkyl chain to which is attached a benzene ring having a sulfonate group (SO₃⁻) in the para position (Figure 1). They are the main material in the formulation of detergents and cosmetics by their functional diversity (detergency, emulsion, solubilization) [1].

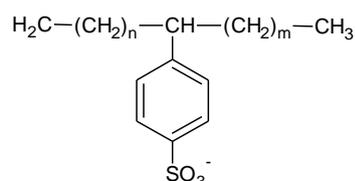


Figure 1: Structure of Linear Alkylbenzenesulfonates (LAS)

This results in a statistical distribution of the benzene ring along the carbon chain, except for terminal carbons [2,3]. For each molecule of given length of the chain, called homologues, there are different isomers according to the position of the carbon on which the phenyl ring is attached. In particular, the homologues C11 and C12, having chains of 11 and 12 carbon atoms respectively (Figs 2 and 3), are widely used for their surfactant properties (detergency, emulsion, solubilization, etc.). Analyzes have determined their proportions in commercial detergents and in raw effluents [4, 5]. The occurrence of these micropollutants in the environment is thus proven. In addition, linear alkylbenzenesulfonates have a major impact on aquatic fauna and flora [6-8]. This work aims to contribute to the effective management of waste soap rich in these pollutants. To do this, the study of the chemical stability of the C11 and C12 isomers from the global indices by the DFT method is carried out. It will identify some solutions for a more ecological use of these micropollutants by manufacturers.

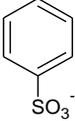
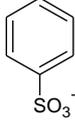
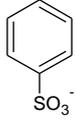
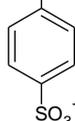
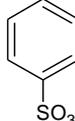
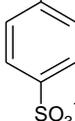
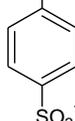
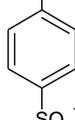
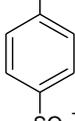
Structure	Name	Code
$\text{H}_3\text{C}-\text{CH}-(\text{CH}_2)_8-\text{CH}_3$ 	4-(2-undécylbenzène) sulfonate	2C11
$\text{H}_3\text{C}-\text{CH}_2-\text{CH}-(\text{CH}_2)_7-\text{CH}_3$ 	4-(3-undécylbenzène) sulfonate	3C11
$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}-(\text{CH}_2)_6-\text{CH}_3$ 	4-(4-undécylbenzène) sulfonate	4C11
$\text{H}_3\text{C}-(\text{CH}_2)_3-\text{CH}-(\text{CH}_2)_5-\text{CH}_3$ 	4-(5-undécylbenzène) sulfonate	5C11
$\text{H}_3\text{C}-(\text{CH}_2)_4-\text{CH}-(\text{CH}_2)_4-\text{CH}_3$ 	4-(6-undécylbenzène) sulfonate	6C11

Figure 2: Isomers of the C11 homologue

Structure	Name	Code
$\text{H}_3\text{C}-\text{CH}-(\text{CH}_2)_9-\text{CH}_3$ 	4-(2-dodécylbenzène) sulfonate	2C12
$\text{H}_3\text{C}-\text{CH}_2-\text{CH}-(\text{CH}_2)_8-\text{CH}_3$ 	4-(3-dodécylbenzène) sulfonate	3C12
$\text{H}_3\text{C}-(\text{CH}_2)_2-\text{CH}-(\text{CH}_2)_7-\text{CH}_3$ 	4-(4-dodécylbenzène) sulfonate	4C12
$\text{H}_3\text{C}-(\text{CH}_2)_3-\text{CH}-(\text{CH}_2)_6-\text{CH}_3$ 	4-(5-dodécylbenzène) sulfonate	5C12

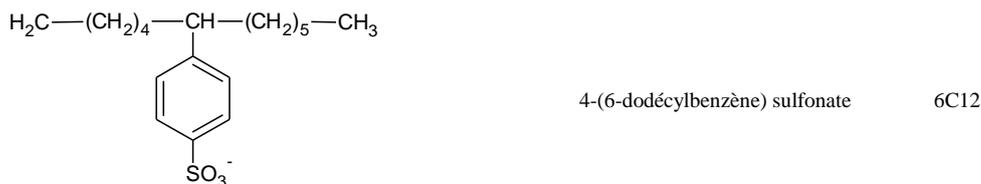


Figure 3: Isomers of the C12

II CALCULATION METHODOLOGIES.

2.1. Method and theoretical level of calculation.

All calculations were performed using the GaussView graphics software and the Gaussian 03 [9] calculation software at the DFT / B3LYP / 6-311G (d, p) level [10]. Each of the isomers was totally optimized with a calculation of frequencies at the above mentioned level, in a vacuum, at first. Subsequently, a single point calculation taking into account the solvation effects (solvent: water, IEFPCM method) on each isomer is performed at the same level of theory. Indeed, the vacuum being the perfect medium, an optimization in this medium will make it possible to obtain the most stable geometry of the molecule. Then, the calculation in single point in the water which is the study matrix, makes it possible to analyze the effects of this medium on the stability of LAS.

2.2. Global stability and reactivity parameters.

The calculated parameters are the energies of the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap ΔE (relation (1)), the chemical potential μ (relation (2)) and the nucleophilicity index N (relation (3))

$$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (1)$$

The chemical potential is determined according to the relationship:

$$\mu = \frac{1}{2}(E_{\text{HOMO}} + E_{\text{LUMO}}) \quad (2)$$

The chemical hardness (η) is defined as the first derivative of the electronic potential with respect to the number of electrons N with external potential $V(r)$ constant [10].

$$\eta = \left(\frac{\partial \mu}{\partial N} \right)_{V(r)} = \left(\frac{\partial^2 E}{\partial N^2} \right)_{V(r)} = \frac{(E_{\text{LUMO}} - E_{\text{HOMO}})}{2} \quad (3)$$

The nucleophilicity index N of a molecule is determined according to [11] from the E_{HOMO} energies obtained by the method of Kohn-Sham [12]. The empirical (relative) nucleophilic index (N) is defined as follows:

$$N = E_{\text{molecule}} - E_{\text{HOMO}}(\text{TCE}) \quad (4)$$

Where $E_{\text{HOMO}}(\text{TCE})$ is the energy of the highest occupied molecular orbital of tetracyanoethylene, $(\text{CN})_2 - \text{C} = \text{C} - (\text{CN})_2$, taken as the reference in the nucleophilicity scale, because it presents the lowest HOMO energy. This reference molecule was fully optimized with a frequency calculation with DFT method at B3LYP / 6-311G (d, p) level in vacuum, at first. Then, a single point calculation taking into account solvation effects (solvent: water, IEFPCM method) is carried out at the same theoretical level.

Calculations give $E_{\text{HOMO}}(\text{TCE}) = -8.879$ eV. The nucleophilic index $N(M)$ of a molecule M is then determined according to the relation:

$$N(M) = E_{\text{HOMO}}(M) - E_{\text{HOMO}}(\text{TCE}) = E_{\text{HOMO}}(M) + 8.879 \quad (5)$$

III RESULTS AND DISCUSSIONS

3.1. Global reactivity indices

The energy descriptor values of the isomers of homologues C11 and C12 are respectively recorded in the following tables I and II:

Table I: Global reactivity indices of C11 homologues isomers calculated at the B3LYP / 6-311G (d, p) level, taking into account the solvation (Solvent: water, IEFPCM).

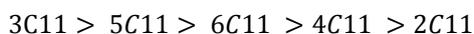
Descriptors	2C11	3C11	4C11	5C11	6C11
E _{LUMO} (eV)	-0,497	-0,455	-0,460	-0,445	-0,444
E _{HOMO} (eV)	-6,603	-6,588	-6,580	-6,576	-6,572
ΔE (eV)	6,106	6,133	6,120	6,131	6,128
μ (eV)	-3,550	-3,522	-3,520	-3,511	-3,508
η (eV)	3,053	3,067	3,060	3,066	3,064
N (eV)	2,276	2,291	2,299	2,303	2,307

Table II: global reactivity indices of C12 homologues isomers calculated at the B3LYP / 6-311G (d, p) level, taking into account the solvation (Solvent: water, IEFPCM).

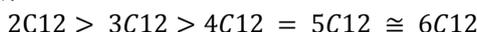
Descriptors	2C12	3C12	4C12	5C12	6C12
E _{LUMO} (eV)	-0,454	-0,445	-0,443	-0,441	-0,441
E _{HOMO} (eV)	-6,607	-6,582	-6,575	-6,573	-6,572
ΔE (eV)	6,153	6,137	6,132	6,132	6,131
μ (eV)	-3,531	-3,514	-3,509	-3,507	-3,506
η (eV)	3,077	3,069	3,066	3,066	3,065
N (eV)	2,272	2,297	2,304	2,306	2,307

3.1.1 The energy gap

The energy gap (ΔE) makes it possible to predict the global reactivity of a molecule. A low energy gap molecule facilitates the electronic transition between the two E_{HOMO} and E_{LUMO} energy levels [13]. The molecule is then less stable and therefore more reactive. The analysis of the results obtained (Table I), shows that the 2C11 isomer has the smallest gap (6,106 eV) while the 3C11 isomer records the highest energy gap (6,133 eV). The 3C11 isomer is therefore the most stable and the 2C11 isomer is the least stable. The order of stability is as follows:



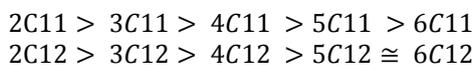
As for the C12 homologue (Table II), the 2C12 isomer has the highest energy gap (6.153 eV) while the 6C12 isomer has the lowest energy gap value (6.131 eV). The 2C12 isomer being the least reactive is therefore the most stable. The 4C12 and 5C12 isomers have the same energy gap (6,132 eV) which differs little from that of 6 C12 (6,131 eV). The order of decreasing stability of the C12 isomers is then determined according to the position of the benzene ring below:



The energy gap of the isomers of the C12 homologue is influenced by the position of the benzene ring on the linear carbon chain. This influence decreases when the benzene ring is closer to the terminal methyl group. The results show that the stability order of the isomers of the C12 homologue differs from that of the isomers of the C11 homologue. The energy gap depends, of course, on the position of the benzene ring, but it is strongly influenced by the length of the carbon chain. Indeed, for the same position of the benzene ring, the C12 isomers have the highest energy gaps. These isomers are more stable than the C11 isomers because they are the least reactive. Moreover, the calculations show that the energy gap decreases with the length of the carbon chain. It should be noted that the 2C12 isomer is more stable than 2C11 because it has the highest energy gap (6.153 eV) than 2C11 (6.106 eV). This energy gap value of 2C12 is also greater than that of 3C11 (6.133 eV). In fact, with an energy gap of 6.153 eV, the 2C12 isomer is the most stable of all isomers of the C11 and C12 homologues.

3.1.2. The chemical potential.

The chemical potential reflects the tendency of the electron cloud of a molecule to escape. It expresses the ability of a molecule to give electrons [14-16]. The 2C11 and 2C12 isomers have respectively the low chemical potential values (-3,550 eV) and (-3,531 eV) (Tables I and II). On the other hand, the 6C11 and 6C12 isomers record the highest respective chemical potentials (-3,508 eV) and (-3,506 eV). Decreasing stability orders are as follows:

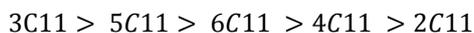


The 2C11 and 2C12 isomers are the most stable and the 6C11, 5C12 and 6C12 isomers are the least stable. The position of the benzene ring influences the charge donor nature of the C11 and C12 LAS derivatives. Depending on the length of the chain, the isomers of the C11 homologue have the lowest chemical potentials. The C11

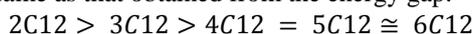
counterpart is the least charge giver than the C12 counterpart. This donor character increases with the length of the alkyl chain.

3.1.3 The chemical hardness

Hardness is the resistance of a molecular system to electron transfer (gain or loss of electrons). It measures the stability of the molecular system. Thus, the higher the hardness of the molecule, the more stable it is. The results from this study (Table I) show that the 3C11 isomer has the highest hardness (3.067 eV) while the 2C11 isomer has the lowest value (3.053 eV). The order of decreasing stability of the C11 isomers is the same as that relating to the energy gap:



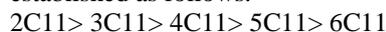
The 3C11 isomer is more resistant to charge transfer than the 2C11 isomer. In terms of electron transition, the 2C11 isomer is less reactive than the 3C11 isomer. This result is perfectly in agreement with that obtained with the energy gap which is related to the hardness. Concerning the C12 isomers (Table II), the order of decreasing stability is also the same as that obtained from the energy gap.



The 2C12 isomer is more resistant to electronic transition than other isomers. This result is in agreement with that relating to the energy gap. The 4C12, 5C12 and 6C12 isomers are the least stable. The hardness depends on the position of the benzene ring on the linear carbon chain. In addition, for the same position of this nucleus, the C12 isomers have the highest hardnesses that the C11 isomers. The hardness increases with the length of the linear carbon chain. The C12 counterpart is more resistant to electronic transfers than the C11 counterpart. The latter is therefore more responsive and less stable.

3.1.4 The nucleophilicity index

The nucleophilicity index reflects the electron donor character of a molecular system. The higher this index is for a molecule, the less stable it is [17,18]. The 2C11 and 2C12 isomers have low nucleophilic index values (2,276 eV) and (2,272 eV) respectively (Tables I and II). On the other hand, the 6C11 and 6C12 isomers have the same highest nucleophilic index (2.307 eV). According to this index the order of decreasing stability is established as follows.



The nucleophilicity index indicates that the 2C11 and 2C12 isomers are the most stable and the 6C11, 5C12 and 6C12 isomers the least stable. This index is also sensitive to the position of the benzene ring as well as to the length of the alkyl chain.

3.2. Influence of the position of the sulfonate substituent on the stability of the 2C11 and 2C12 isomers.

This study concerns the specific case of the stable isomers 2C11 and 2C12. When the sulphonate substituent is in the meta position, they are named respectively m2C11 and m2C12. These isomers are presented hereinafter (Figs. 4 and 5).

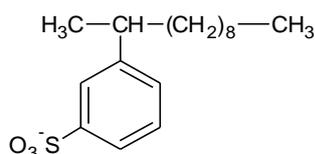


Figure 4: Structure of m2C11: 3-(2-undécylbenzène) sulfonate

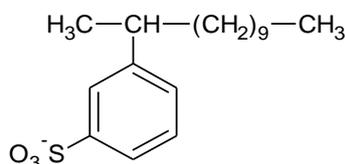


Figure 5: Structure of m2C12: 3-(2-dodécylbenzène) sulfonate

In order to analyze the influence of the position of the substituent on the chemical stability of the linear alkylbenzenesulfonate isomers m2C11 and m2C12, the same overall indices given above are calculated under the same conditions and with the same level of theory as previously. The results obtained for these two series of calculations are recorded in the table below (Tables III).

Table III: Global reactivity indices of the mC11 and mC12 isomers calculated at the B3LYP / 6-311G (d, p) level, taking into account the solvation (Solvent: water, IEFPCM).

Descriptors	E _{LUMO} (eV)	E _{HOMO} (eV)	ΔE (eV)	μ (eV)	η (eV)	N (eV)
m2C11	-0,542	-6,707	6,165	-3,625	3,083	2,172
2C11	-0,497	-6,603	6,106	-3,550	3,053	2,276
m2C12	-0,542	-6,708	6,166	-3,325	3,083	2,171
2C12	-0,454	-6,607	6,153	-3,531	3,077	2,272

The analysis of the results reveals that all calculated global indices vary when the substituent is in a meta position. By way of examples, the energetic gap (ΔE) of the 6,106 eV isomer 2C11 increases to 6,165 eV for the m2C11 isomer (Table III). As for the hardness (η), its value goes from 3.053 eV to 3.063 eV respectively for the isomers 2C11 and m2C11 (Table III). These variations in values are observed at the level of all the indices and isomers studied (Table III). It can therefore be said that the position of the sulphonate substituent in the meta position has an influence on the overall indices of the isomers of linear alkylbenzenesulphonates at 2C11 and 2C12. The variation of an overall reactivity index due to the change of position of the sulphonate substituent was determined according to relation (6):

$$\Delta I = I_{\text{meta}} - I_{\text{para}} \quad (6)$$

In this relation, I is the index; I_{para} the index calculated when the substituent is in the para position; I_{meta} is the index calculated when the substituent is in the meta position. Variations in the values of the different global descriptors are recorded in Table IV.

Table IV: Influence de la position méta du substituant sulfonate sur les indices globaux

	ΔE (eV)	μ (eV)	η (eV)	N (eV)
ΔI _{2C11} (eV)	+0,059	-0,075	+0,030	-0,104
ΔI _{2C12} (eV)	+0,013	+0,206	+0,006	-0,101

The meta position of the sulphonate substituent increases the energy gap of (+0.059 eV), the hardness of (+0.030 eV), of the isomer 2C11 and leads to a decrease in the potential (-0.075 eV) as well as the nucleophilic index of (-0.104 eV). The meta position of the sulfonate group enhances the stability of the 2C11 isomer. With regard to the 2C12 isomer, the influence is not significant on the energy gap and the hardness with small variations of these parameters respectively (+0.013 eV) and (+0.006 eV) while the nucleophile index decreases slightly (-0.101 eV). According to these indices, the stability of 2C12 increases with the meta position of the sulphonate substituent. On the other hand, while the meta position of the substituent decreases the chemical potential of the 2C11 isomer, that of the 2C12 isomer increases strongly by (+0,206 eV). The meta position of the substituent significantly increases the donor character of the 2C12 isomer thus rendering it more reactive and less stable. This strong increase in this m2C12 donor character is therefore related to the length of the linear carbon chain. Overall, the meta-sulphonate substituent enhances the stability of the 2C11 and 2C12 isomers, making the most stable m2C11 and m2C12 isomers.

IV CONCLUSION.

This work reveals that isomers of linear alkylbenzenesulfonates have different stabilities depending on the position of the benzene ring on the linear carbon chain and the length of this carbon chain. Specifically, the benzene ring on the second carbon gives these isomers a high stability relative to the other isomers. Moreover (In addition), the meta position of the sulfonate substituent on the benzene ring enhances the stability of the 4-(2-undecylbenzene) sulfonate and 4-(2-dodecylbenzene)sulfonate isomers, chosen for their particular stability. For more environmentally friendly management of linear alkylbenzenesulfonates, the use of stable isomers is recommended. Because they are better predisposed to treatment because they are stable and easily manipulated. The synthesis of these isomers by manufacturers of soap is recommended, especially the isomers 3-(2-undecylbenzene) sulfonate and 3-(2-dodecylbenzene) sulfonate.

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