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Theoretical study on the electronic structure of triphenyl sulfonium salts: Electronic excitation and electron transfer processes

Ioannis D. Petsalakis [a],*, Giannoula Theodorakopoulos [a], Nektarios N. Lathiotakis [a],
Dimitra G. Georgiadou [b], Maria Vasilopoulou [b], Panagiotis Argitis [b]

[a] *Theoretical and Physical Chemistry Institute, The National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, 116 35 Athens, Greece*
[b] *Institute of Microelectronics, NCSR 'Demokritos', 15310 Athens, Greece*

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ABSTRACT

Density functional theory (DFT) and Time Dependent DFT calculations on triphenyl sulfonium cation (TPS) and the salts of TPS with triflate, nonaflate, perfluoro-1-octanesulfonate and hexafluoro antimonate anions are presented. These systems are widely used as cationic photoinitiators and as electron ejection layer for polymer light-emitting diodes. While some differences exist in the electronic structure of the different salts, their lowest energy intense absorption maxima are calculated at nearly the same energy for all systems. The first excited state of TPS and of the TPS salts is dissociating. Electron addition to the TPS salts lowers their energy by 1.0–1.33 eV.

1. Introduction

Triphenyl sulfonium (TPS) salts are well known ionic compounds, widely applied in the past decades in photoresist technology either as photoinitiators of cationic polymerizations or as photoacid generators in chemically amplified lithography systems [1,2]. Their functionality is based on their direct or sensitized photolysis, which induces the cleavage of the C–S bond in the triphenyl sulfonium cation and the subsequent release of a reactive proton, which in turn induces solubility-changing reactions, such as acid catalyzed cleavage or cationic polymerization/cross-linking in polymeric matrices [3]. The photoacid-generation function of the sulfonium salts has been also exploited for promoting desirable changes of properties of materials, as for instance, the conductivity in poly-aniline films [4] or the dielectric properties of organic films used in radiation sensors [5]. Moreover, sulfonium salts have been involved in organic optoelectronic applications, especially in OLEDs technology, in order to facilitate stacked device fabrication [6] or RGB definition [7]. The role of selected salts of this family, in particular triphenyl sulfonium triflate and nonaflate, in the device performance has been investigated, when incorporated in the green emitting conjugated copolymer poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-{2,1,3}-thiadiazole)] (F8BT) [8] or in the blue emitting poly[2-(6-cyano-6-methyl-heptyloxy)-1,4-phenylene] (CN-PPP) [9]. It was shown that addition of these salts can increase the luminescence and decrease the turn-on and operating voltage, thus considerably improving device performance. Although the nature of the anion does not seem to influence the photosensitivity of TPS-salts, their size is critical to their reactivity when applied as photoinitiators of cationic polymerizations [10] and, more importantly, it has been found that it may also affect the injection, transport and emission properties of organic light-emitting diodes [11]. Recently sulfonium salts bearing different counter-anions were introduced as spin-coatable all-organic cathode interfacial layers (CILs), improving substantially the luminous efficiency and brightness of F8BT-based PLEDs [12]. This improvement was attributed mainly to the favourable decrease of the polymer/Al injection barrier, which was also assisted by the conduction of electrons through the triphenyl sulfonium salt sites. These recent studies necessitated a more detailed theoretical analysis of the electronic structure of sulfonium salts.

The dissociation of TPS salts upon electronic excitation leading to photoacid generation and the dissociative reduction of the TPS cation have been previously studied [13,14] and rationalized in terms of the character of the highest occupied (HOMO or H here) and lowest unoccupied (LUMO or L here) molecular orbitals of the cation, according to semiempirical, AM1, calculations [15]. These rationalizations have been generally invoked in subsequent reports [16], but it should be noted that the labels σ^* and π^*, employed in [15], are not appropriate in the absence of a plane of symmetry in the TPS cations. In our previous publication [12] we have presented some preliminary results from calculations on the anionic forms of TPS-triflate and TPS-nonaflate, i.e., [TPS-triflate]$^-$ and [TPS-nonaflate]$^-$, to rationalize the functionality of these TPS salts as cathode interfacial layers (CILs). It was found that

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* Corresponding author. Fax: +30 210 7273794.
E-mail address: idpet@eie.gr (I.D. Petsalakis).

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the acquisition of an electron by TPS salts lowers their total energy with respect to the neutral, rendering them attractive compounds to be used as electron injecting layers. The effect of stabilisation of sulfonium salts upon electron addition has been also reported by Endo and Tagawa [17], since improving the efficiency of photoacid generators is critical for increasing sensitivity of EUV resists [18]. However, no distinction on the stability of the isolated cation versus the cation in the presence of the anion was made.

In the present report, theoretical calculations are presented on the electronic structure of four TPS salts, differing in the degree of fluorination, chemical nature (organic/inorganic) and size of the anions, namely hexafluoro antimonate, triflate, nonaflate and PFOS. The ground and excited electronic states of the neutral and anionic forms are calculated in an effort to determine the effect of the different counter anions on the electronic structure of the salt.

2. Calculations

The method of calculation employed is DFT [19] for the ground electronic states and TDDFT [20] for the excited, both in conjunction with the M062X [21] functional, which has been reported to perform well for weak interactions and for non-covalent bonding [21] and it has been also found to be the case in previous work by the present authors [22]. In addition, the B3LYP functional [23,24] and the long-range corrected functionals CAM-B3LYP [25] have been employed for some of the calculations, see below, for comparison with the M062X results. While some preliminary calculations employed the 6-31G (d,p) basis set, all the other calculations, except where otherwise stated in what follows, employed basis set 6-311+G (d,p), provided by GAUSSIAN 09 [26]. For Sb the LAN2DZdp ECP basis set [27] was employed.

Geometry optimization DFT calculation have been carried out on the ground electronic state of the TPS cation and the neutral salts of TPS with the anions hexafluoro antimonate, trifluoromethanesulfonate (triflate), perfluoro-1-butanesulfonate (nonaflate) and perfluoro-l-octanesulfonate (PFOS). The optimum ground state structures calculated in the present work, are given in Figure 1. Frequency calculations ensured that these structures are indeed energy minima, while some variations in the starting geometries lead to the same optimum structures.

The excited states were calculated at the ground state minimum geometry and are relevant to the absorption spectra, by TDDFT/M062X and for the TPS-triflate salt by TDDFT/B3LYP and TDDFT/CAM-B3LYP as well. Subsequent geometry optimization of the lowest excited state in each case was carried out by TDDFT/MO62X in order to obtain information on the geometry of the excited state of each system.

3. Results and discussion

The TPS cation was calculated first, cf. (i) in Figure 1, and found to be non-planar in the ground electronic state. The absorption spectrum of the cation obtained by TDDFT is given in Figure 2i (see also below), however, geometry optimization of the first excited state did not converge to a stable geometry but indicated a dissociated system. Similarly, the lowest excited state of the neutral salts (ii)–(v) in Figure 1, obtained by TDDFT calculations, are found to be dissociating. However, even though addition of an electron to the cation leads to its dissociation, in agreement with the previous reports on the dissociative reduction of aryl- and alkyl–aryl TPS cations [13,14], addition of an electron to the salts (ii)–(v) leads to stable structures for the resulting anions, at lower energy than the corresponding neutral salt, as will be described in detail below. This result has been found to be critical when these compounds are used as electron injecting layers in organic optoelectronic devices [12].

3.1. Absorption spectra

The absorption spectra of systems (i)–(v), calculated by TDDFT/M062X at the ground-state geometry are shown in Figure 2 while in Table 1 the results are summarized in terms of λ_{max}, f-values for the transitions from the ground state and the most significant excitations characterizing the excited state. As shown in Figure 2i for the TPS cation, significant absorption probability is found at 222

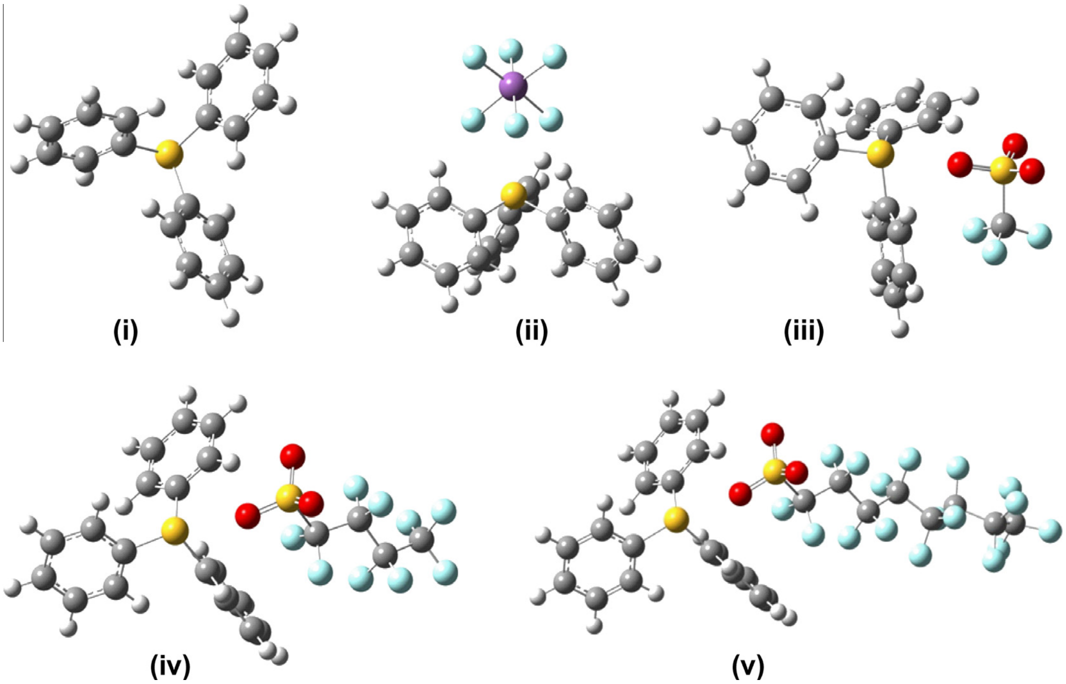

Figure 1. Ground-state optimized geometries for TPS cation (i) and the salts with hexafluoro-antimonate (ii), triflate (iii), nonaflate (iv) and PFOS (v).