2332 *J. Phys. Chem. A* **2004,** *108,* 2332−2338

Rotational Barriers, Charges, and Spin Densities in Alkyl Aryl Sulfide Radical Cations: A Density Functional Study

Enrico Baciocchi and Maria Francesca Gerini*

Università degli Studi di Roma "La Sapienza", P. le A. Moro 5, 00185, Roma, Italy

Received: September 11, 2003; In Final Form: December 16, 2003

The structures and the torsional potentials for the rotation around the aryl−SR bond of a series of neutral alkyl aryl sulfides and their corresponding radical cations were studied by applying density functional theory at the B3LYP/6-311G** level. In all radical cations the most stable conformer corresponds to the structure in which the S-alkyl group is in the planar conformation, with sulfur and alkyl atoms coplanar with the aromatic ring. The rotational energy barriers were relatively high, ranging from 12.307 to 19.496 kcal/mol. In all cases substantial geometrical changes with respect to the parent sulfide were observed, the radical cation presenting a quinoidic structure, with quasi-single bonds alternating to quasi-double bonds, and a shorter C_{Ar}−S bond. These results illustrate the importance, in the radical cation, of the conjugation between the sulfur atom and the aromatic π system. Such a conjugation is not so important in the neutral molecules and in fact the energy minimum for alkyl phenyl sulfides is located in correspondence of the perpendicular form, with the exception of thioanisole for which the two effects seem to have a similar role. Calculation of Mulliken spin populations, MK and NPA charges showed that $PhSR^{\bullet+}$ and $4\text{-}NCC_6H_4SR^{\bullet+}$ are mainly sulfur-centered radical cations, whereas $4\text{-}Me_2NC_6H_4SMe^{\bullet+}$ and $4\text{-}MeOC_6H_4SMe^{\bullet+}$ are essentially aromatic radical cations with some charge and spin density at the sulfur atom. Ionization energies were also calculated for both the planar and perpendicular forms; for the PhSR series (particularly in the former case), they resulted in good agreement with the experimental ones.

Introduction

In aromatic sulfides (ArSR) there is an important conformational problem related to the rotation around the C_{Ar}−SR bond. If ϕ is defined as the dihedral angle between the aromatic ring and the C_{Ar}−S−R plane ($\phi = R{-}S{-}C_{Ar1}{-}C_{Ar2}$), two limit conformations are possible: one at $\phi = 0°$ or $180°$, which corresponds to the $S{-}C_{Alk}$ bond coplanar with the aromatic ring and one at $\phi = 90°$, where the $S{-}C_{Alk}$ bond is orthogonal to the aromatic ring (through the text these forms will be referred to as the planar and perpendicular forms, respectively). The conformational equilibrium results from a balance between the conjugative effect (interaction between the sulfur lone pair and the aromatic π system), which is at a maximum in the planar form and absent in the perpendicular one and the steric effect (interaction of the R group with the ortho hydrogen atom of the aromatic ring), which is higher in the planar form than in the perpendicular one. In several neutral molecules, information on the relative weight of the two conformers and the rotational energy barrier (i.e., the energy difference between the planar and the perpendicular conformers) has been determined by PES measurements[1−3] as well as by theoretical calculations.[3,4]

A different situation appears to hold for the corresponding aromatic sulfide radical cations. ESR experiments indicate that the planar conformation is the predominant one, which means that the conjugation between the sulfur and the aromatic π system in the radical cation is much more important than the steric interactions. The barrier to the rotation has been estimated to be quite high but only limit values are reported.[5] Nor is detailed information available concerning the charge and spin distribution in the radical cations and how such a distribution depends on the rotation around the C_{Ar}−S bond. This information is of great importance because the reactivity of the radical cation, which is strictly related to the charge and spin distribution, is subject to stereoelectronic requirements.

There is great and continuous interest for the properties of radicals and radical ions derived from sulfur containing compounds due to the fact that these species are involved in a large variety of chemical processes, extending from those of industrial importance (i.e., conducting polymers[6]) to the biological ones (i.e., enzymatic oxidation of organic sulfides[7]). Thus, we felt it worthwhile to carry out DFT calculations aimed at obtaining data on the conformational equilibria, energy barriers for the internal rotation, geometry, charge, and spin distributions on a series of alkyl phenyl sulfide radical cations ($PhSR^{\bullet+}$, R = Me, Et, *i*Pr, *t*Bu). The effect of electron donor (NMe_2 and OMe) and electron acceptor (CN) ring substituents was also determined. To the best of our knowledge, DFT calculations have so far been performed only on thioanisole radical cation.[8]

The DFT method was chosen because it provides results for open-shell species that are often in better agreement with the available experimental data than HF or MP2 calculations.[9] This makes DFT calculations attractive with respect to the very costly coupled cluster and quadratic configuration interaction methods. For comparison, DFT calculations were also performed on the corresponding neutral substrates. Whenever possible, the results of calculations were compared with the corresponding experimental data.

Computational Methods

All computations were performed with the Gaussian 98 program.[10] Potential barriers for internal rotations of the neutral

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* Corresponding author. Tel: +39-06-49913682. Fax: +39-06-490421. E-mail: francesca.gerini@uniroma1.it.

10.1021/jp0367124 CCC: $27.50

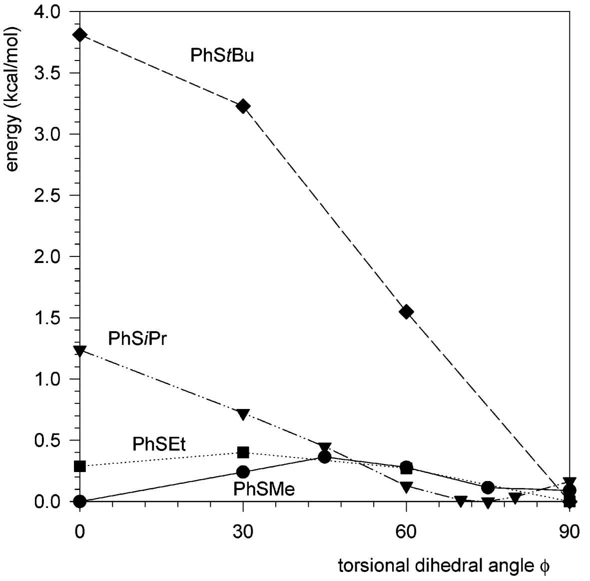


Figure 1. Energy profile for the internal rotation about the C_{Ar}−S bond in PhSMe (circles), PhSEt (squares), PhS*i*Pr (triangles), and PhS*t*Bu (diamonds).

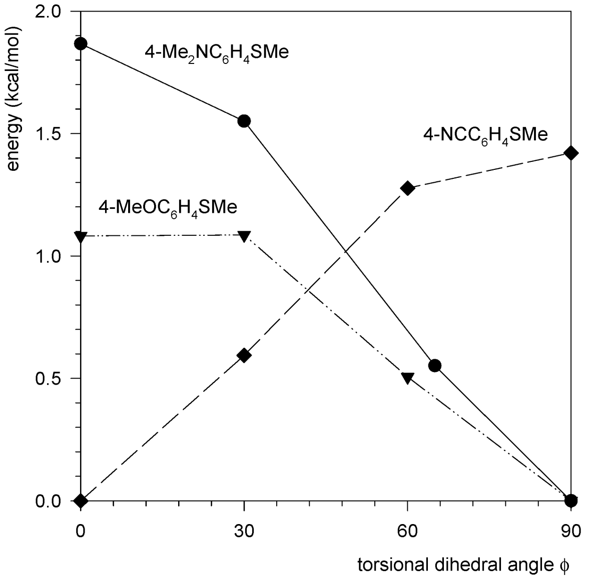


Figure 2. Energy profile for the internal rotation about the C_{Ar}−S bond in 4-$Me_2NC_6H_4SMe$ (circles), 4-$MeOC_6H_4SMe$ (triangles), and 4-NCC_6H_4SMe (diamonds).

and cationic compounds were calculated using the three-parameter hybrid functional B3LYP[11,12] with the 6-311G** basis set.[13] Such functional was chosen because it is reported to yield accurate geometries and reasonable energies.[14−17]

The potential energy for the internal rotation was calculated as a function of the dihedral angle ϕ (ϕ = R−S−C_{Ar1}−C_{Ar2}) by varying it by steps of 30° (or for some molecules at shorter intervals to better define the shape of the potential barrier) and allowing the other parameters to be optimized. The minima and maxima on the torsional potential were optimized. Harmonic vibrational frequencies were calculated at the B3LYP/6-311G** level to confirm that optimized structures correspond to local minima and to determine zero-point energy (ZPE) corrections. The analysis of the vibrational frequencies found that all the radical cations perpendicular conformers were first-order saddle points on the energy hypersurface. The barriers for internal rotations were calculated as the differences between the total energy of each conformation and that of the most stable conformer.

Spin contamination due to states of multiplicity higher than the doublet state was negligible; the value of the $\langle S^2 \rangle$ operator was, in all cases, well within 5% of the expectation value for a doublet (0.75).

The atomic charges were derived by using either electrostatic potential (ESP)-driven charges according to the Merz−Singh−Kollman (MK) scheme[18,19] and the natural population analysis (NPA). Unpaired electron spin densities were calculated using the Mulliken population analysis.

Results

Neutral Sulfides. The B3LYP/6-311G** calculations on neutral PhSMe located the energy minima on the potential function of the internal rotation about the C_{Ar}−S bond at the planar (absolute minimum) and at the perpendicular (relative minimum) conformations, $\phi = 0°$ and $\phi = 90°$, respectively, and gave a difference between these two conformations of 0.090 kcal/mol (Figure 1 and Table 1S), thus showing that the two forms have practically the same energy. The conformation around 45° has the maximum energy and the rotational energy barrier is 0.363 kcal/mol.

A different situation was found for the other PhSR (R = Et, *i*Pr, *t*Bu) (Figure 1 and Tables 2S−4S). For all these sulfides, calculations indicated that the planar form has a higher energy than the perpendicular one, the difference in energy between the two conformers increasing, as expected, with the bulkiness of the R group (interaction with the ortho H of the aromatic ring). The values (kcal/mol) were 0.288 for R = Et, 1.074 for R = *i*Pr, and 3.810 for R = *t*Bu. The energy barriers (kcal/mol) to be overcome to convert the perpendicular into the planar form were 0.400 (R = Et), 1.238 (R = *i*Pr), and 3.810 (R = *t*Bu). In the latter case the energy barrier coincides with the difference in energy between the planar and the perpendicular form.

It can also be noted that modest geometric changes occur on going from the planar to the perpendicular form (Tables 1S−4S). The most significant ones are the increase of the C_{Ar}−S, S−C_{Alk}, and C_{Ar2}−H (oriented toward the S−R group) bond lengths and the decrease of both the angles C_{Ar2}−C_{Ar1}−S and C_{Ar}−S−C_{Alk}. For example, in the case of PhSMe the length of C_{Ar}−S bond goes from 1.785 to 1.800 Å, that of the S−C_{Alk} bond from 1.820 to 1.835 Å, and that of the C_{Ar2}−H bond from 1.082 to 1.084 Å. At the same time, the C_{Ar2}−C_{Ar1}−S angle decreases from 124.5° to 120.1° and the C_{Ar}−S−C_{Alk} angle passes from 103.7° to 100.5°. A similar situation holds for the other PhSR molecules, with the largest variations observed for R = *t*Bu.

The effect of the introduction of a *para* ring substituent (X = NMe_2, OMe, CN) on the ArSMe conformational equilibrium was also studied (Figure 2 and Tables 5S−7S). The calculations show that the introduction of an electron donating group (EDG) clearly favors the perpendicular conformer, which is the absolute minimum in energy, whereas the planar form is the maximum. Such an effect is larger with X = NMe_2 than with X = OMe. Accordingly, the perpendicular conformer is more stable than the planar one by 1.867 kcal/mol in the former case and by 1.082 kcal/mol in the second case.[20] The barrier for the internal rotation coincides with these differences. Interestingly, the reverse situation holds when the ring substituent is an electron withdrawing group (EWG). When X = CN we found an increase in the energy with increasing torsional dihedral angle from 0° to 90°. Thus, the perpendicular conformer is the

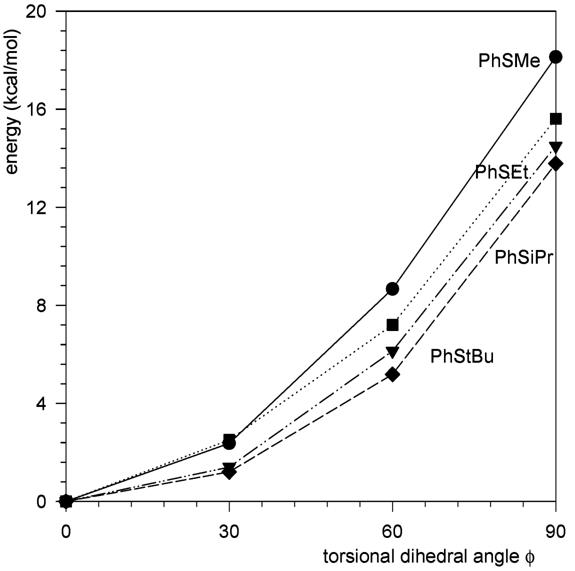


Figure 3. Energy profile for the internal rotation about the C_{Ar}−S bond in in PhSMe$^{\bullet+}$ (circles), PhSEt$^{\bullet+}$ (squares), PhS*i*Pr$^{\bullet+}$ (triangles), and PhS*t*Bu$^{\bullet+}$ (diamonds).

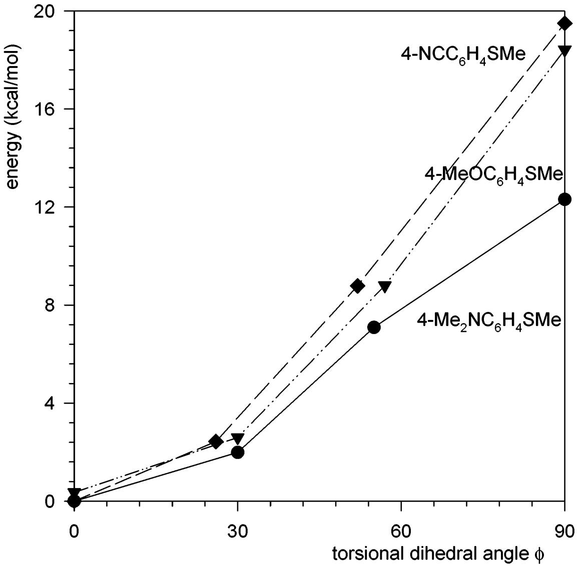


Figure 4. Energy profile for the internal rotation about the C_{Ar}−S bond in 4-$Me_2NC_6H_4SMe^{\bullet+}$ (circles), 4-$MeOC_6H_4SMe^{\bullet+}$ (triangles), and 4-$NCC_6H_4SMe^{\bullet+}$ (diamonds).

maximum on the potential function and the energy barrier for the rotation is 1.421 kcal/mol.

Upon rotation around the C_{Ar}−S bond all the three substituted thioanisoles showed the occurrence of modest geometric changes (Tables 5S−7S), which are of the same nature as those found for the unsubstituted sulfides.

Sulfide Radical Cations. As shown by data reported in Figures 3 and 4 and in Tables 8S−14S for all the radical cations investigated, the planar conformation is the predominant one. The energy always increases as the value of the dihedral angle increases from 0° to 90°, and only a very deep energy minimum on the potential function of the internal rotation about the C_{Ar}−S bond corresponding to the planar form has been found. The perpendicular conformation is at a maximum in energy. The energy difference between the planar and perpendicular conformation is always very high, ranging in the PhSR$^{\bullet+}$ series from 18.131 kcal/mol for PhSMe$^{\bullet+}$ [21] to 13.783 kcal/mol for PhS*t*Bu$^{\bullet+}$.

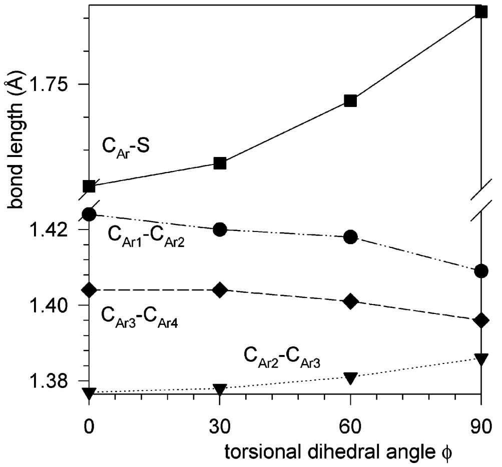


Figure 5. Bond lengths in PhSMe$^{\bullet+}$ as a function of the torsional dihedral angle ϕ.

In the ring-substituted systems (4-$XC_6H_4SMe^{\bullet+}$) the energy differences between the planar and the perpendicular form are 19.496 kcal/mol for X = CN, 18.418 kcal/mol for X = OMe,[22] and 12.307 kcal/mol for X = NMe_2.

All the sulfide radical cations exhibit significant geometric changes on going from the planar to the perpendicular form as well as with respect to the parent sulfides. In particular, the planar radical cations present a distorted geometry of the aromatic ring, with quasi-single bond alternating to quasi-double bond, i.e., for PhSMe$^{\bullet+}$ the C_{Ar1}−C_{Ar2} bond length is 1.424 Å, the C_{Ar2}−C_{Ar3} bond length is 1.377 Å, and the C_{Ar3}−C_{Ar4} bond length is 1.404 Å. For PhSMe these values are 1.398, 1.392, and 1.394 Å, respectively. Moreover, the C_{Ar}−S bond length significantly decreases in the radical cation, i.e., to 1.719 Å for PhSMe$^{\bullet+}$, compared to 1.785 Å for the neutral sulfide. Upon increasing the torsional dihedral angle, that is on going toward the perpendicular form, we observed a regular modification of the bond lengths, restoring the normal geometry of the aromatic ring. As an example, we report the observed trends for PhSMe$^{\bullet+}$ in Figure 5. All the other sulfides exhibit a similar behavior. The increase of the C_{Ar}−S and C_{Ar2}−C_{Ar3} bond lengths and the parallel decrease of the C_{Ar1}−C_{Ar2} and C_{Ar3}−C_{Ar4} bond lengths are particularly evident. As the bulkiness of the alkyl group is increased, the C_{Ar2}−C_{Ar1}−S and C_{Ar}−S−C_{Alk} angles are progressively more distorted in the planar form to become 126.8° and 114.3°, respectively, for PhS*t*Bu$^{\bullet+}$.

From the data collected in Tables 1S−14S, it is possible to calculate the adiabatic ionization energy (IE), that is the difference between the total energy of the optimized neutral and that of the radical cation, with or without the correction of the ZPE. The data for the alkyl phenyl sulfide series are collected in Table 1 where the available experimental values are also reported.

MK and NPA charges and Mulliken spin populations for the planar and perpendicular conformations of the radical cations were also calculated. In Chart 1 MK charges and Mulliken spin populations are reported for the PhSR$^{\bullet+}$ series, in Chart 2 for the para-substituted thioanisole radical cations. Charges derived from the NPA are collected in Chart 1S.

Discussion

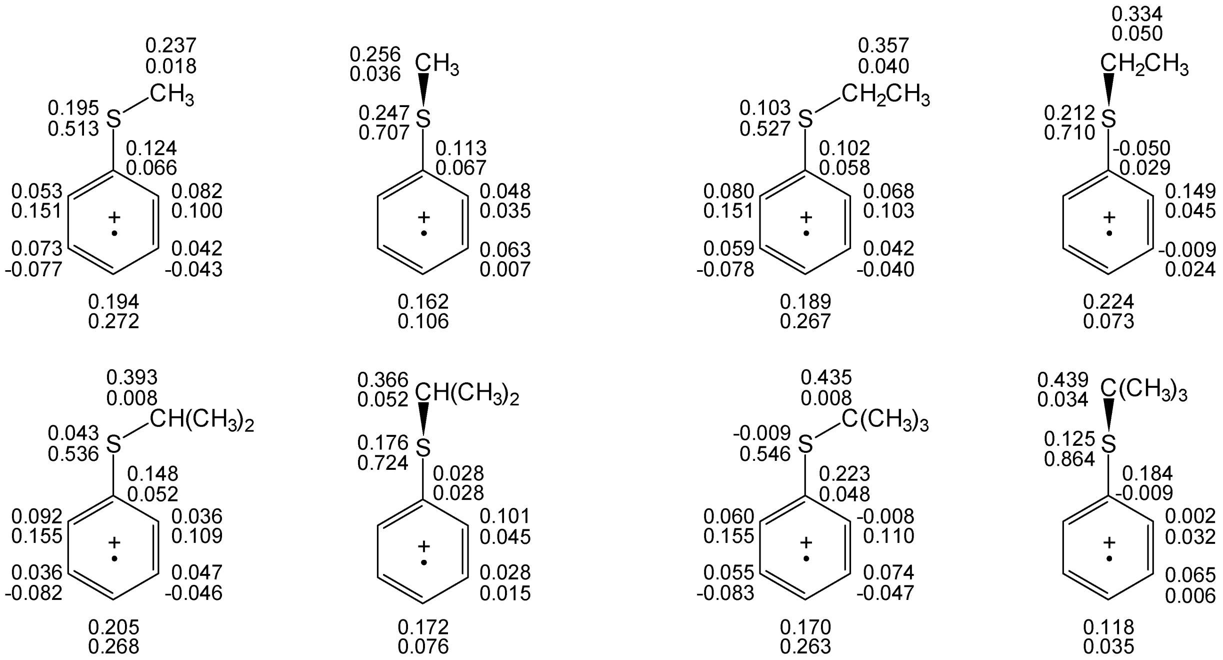
Neutral Sulfides. As already mentioned, the conformation of the ArSR molecules is controlled by two major opposite factors that determine the most stable conformation and the height of the energy barrier for the internal rotation. The

TABLE 1: Experimental and Calculated (with and without ZPE) IEs for the Planar and the Perpendicular PhSR Conformers and Redox Potentials for the $PhSR^{•+}$/PhSR Couples.

R	IE planar (exp)	IE perpendicular (exp)	IE planar (calc)[a]	IE perpendicular (calc)[a]	$E°$ (V) in MeCN vs NHE[b]
Me	7.92[c]−8.01[d]−8.07[e,f]	8.55[g]−8.60[e]	7.70 (7.70)	8.49 (8.44)	1.43
Et	8.00[e,f]	8.53[e]	7.61 (7.60)	8.29 (8.27)	1.46
*i*Pr	8.00[f]	8.46[e]	7.53 (7.52)	8.20 (8.16)	1.49
*t*Bu		8.36[d]−8.40[e,f]	7.44 (7.44)	8.21 (8.20)	1.62

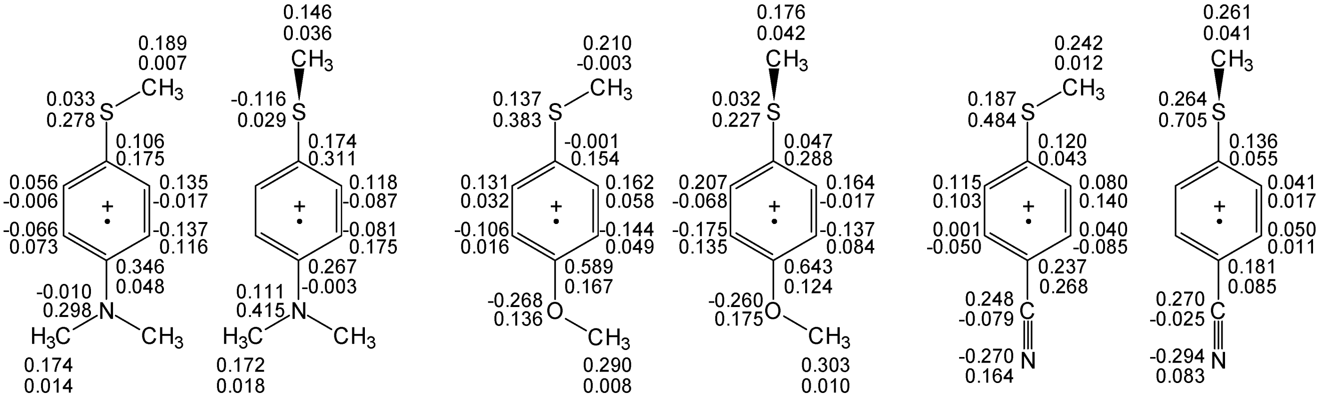
[a] In parentheses is reported the IE value with the ZPE correction. [b] Reference 23. [c] Reference 24. [d] Reference 2. [e] Reference 1. [f] Reference 25. [g] Reference 4.

CHART 1: MK Charges (Upper Lines) and Mulliken Spin Populations (Lower Lines) for the $PhSR•^{+}$ Series[a]



[a] Hydrogen atoms are summed into the attached carbon atoms.

CHART 2: MK Charges (Upper Lines) and Mulliken Spin Populations (Lower Lines) for $4\text{-}XC_6H_4SMe•^{+}$ (X = NMe_2, X = OMe, and X = CN)[a]



[a] Hydrogen atoms are summed into the attached carbon atoms.

electronic effect of the conjugation of the p lone pair of the S atom with the π−system of the aromatic ring increases the stability of the planar form, whereas the steric interaction between the R group and the *ortho*-H atom of the aromatic ring increases the stability of less strained perpendicular form.

In the PhSR series, the calculated differences in energy between the planar and the perpendicular conformer (Tables 1S−4S) allow us to determine the relative amounts of the perpendicular and planar conformer for the various R groups. The data are reported in Table 2 where they are compared with the corresponding experimental values obtained by PES experiments.

The agreement is very good for R = Et, *i*Pr, and *t*Bu. A discrepancy, however, exists for R = Me, because PES experiments indicate a predominance of the planar form, whereas DFT calculations suggest a similar proportion of the

TABLE 2: Calculated and Experimental Abundance of the Perpendicular Conformer for PhSR.

R	% perpendicular conformer (calc)	% perpendicular conformer (exp)[a]
Me	46	10
Et	62	60
*i*Pr	86	85
*t*Bu	99	95

[a] Reference 1.

two conformers. It would therefore seem that for PhSMe DFT calculations underestimate the small difference in stability (about 1.3 kcal/mol from PES experiments) between the two conformers. In this respect, it should be noted that our calculated rotation barrier for PhSMe (0.363 kcal/mol) is also lower than that (1.2−1.4 kcal/mol) estimated by long-range NMR coupling constants.[26,27] However, despite these differences, DFT calculations appear to afford a better description of PhSMe as compared to HF[3,4,24] and MP2[4] calculations, which both predict the perpendicular conformation as the most stable one.

Clearly, our calculations substantially confirm that the conformational equilibrium in the PhSR series is mainly determined by steric effects, the conjugation of the p lone pair of the S atom with the π−system playing a secondary role.

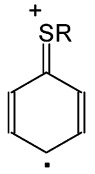
Interestingly, the introduction of a para ring substituent in PhSMe has an effect that depends on whether it is an EDG or an EWG (Figure 2). Thus, the presence of NMe_2 and OMe (EDGs) as para substituents significantly increases the preference for the perpendicular conformation. This effect is stronger with NMe_2 than with OMe. Such behavior is probably due to the fact that, in the presence of a strong electron donating substituent, there is certainly less demand in the planar conformation for sulfur aromatic ring conjugation and the electronic repulsion between the p-electron pair of the sulfur atom and the π−system of the aromatic ring (which is more electron rich than the unsubstituted system) becomes the dominating factor. The rotation around the ϕ dihedral leads to a relief of such a repulsion, and thus the perpendicular conformer becomes the most stable one.

In contrast, a para CN group, which is electron withdrawing, favors the planar conformation. Evidently, in this case, the decreased electron density on the aromatic ring increases the demand for conjugative electron donation from the SMe group and decreases the S−π aromatic ring repulsion. Thus, the planar conformation becomes the more stable one. Qualitatively similar conclusions were made by Distefano and associates[28] on para-substituted α-phenylthioacetonitriles on the basis of PES spectra and STO-3G calculations, which confirms the predictive power of DFT calculations.

Sulfide Radical Cations. DFT calculations have clearly shown that in all alkyl aryl sulfide radical cations the planar conformation is by far the most stable one, thus fully confirming previous conclusions drawn from the analysis of ESR spectra of poly(alkylthio)benzene radical cations.[5] Clearly, the removal of an electron from the alkyl aryl sulfide appears to have a drastic effect on the conformational equilibrium. Through calculations, rotational barriers have also been determined, and they are significantly high, being in the range 12−19 kcal/mol (Figures 3 and 4). Interestingly, on the basis of ESR experiments a value greater than 10 kcal/mol had been assigned to the rotational barrier in 1,4-bis(isopropylthio)benzene radical cation.[5]

Thus, contrary to what is observed for the neutral sulfides, the most important factor governing the conformational equilibrium in the sulfide radical cations is the conjugation between the sulfur atom and the aromatic ring. This makes the energy for the planar conformer, where such conjugation is possible, much lower than that of the perpendicular one, which does not allow any conjugation.

The importance of such a conjugation in the radical cation is also evidenced by the geometry features of the sulfide radical cations (Tables 8S−14S). Accordingly, it can be noticed that in all cases the planar form of the radical cation presents a quinoidic structure, with quasi-single bonds alternating to quasi-double bonds (the $C_{Ar1}-C_{Ar2}$ and $C_{Ar3}-C_{Ar4}$ bond lengths being longer than the $C_{Ar2}-C_{Ar3}$ bond length; i.e., in planar $PhSMe^{\bullet+}$ the lengths are 1.424, 1.404, and 1.377 Å, respectively). Moreover, the $C_{Ar}-S$ bond of the radical cation is significantly shorter than that of the parent sulfide (i.e., 1.719 Å for $PhSMe^{\bullet+}$ and 1.785 Å for PhSMe), the latter finding being a further indication of the S-aromatic ring conjugation. These observations suggest an important contribution of structure **1** to the resonance hybrid of the radical cation.



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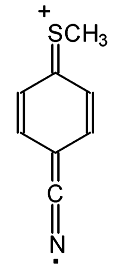
As expected, upon rotation about the dihedral angle from 0° to 90°, the overlap of the S orbital with the π aromatic ring system decreases. The $C_{Ar}-S$ bond length increases and the overall molecular geometry of the perpendicular conformer loses its quinoidic appearance and becomes much similar to that of the parent sulfide (Figure 5).

Another notation is that in the series of alkyl phenyl sulfide radical cations the rotational barrier decreases in the order Me > Et > *i*Pr > *t*Bu, that is by increasing the steric requirement of the R group (Figure 3). This order can be reasonably explained by considering that the planar conformation is subject to a steric strain, which is expected to increase, as seen with the neutral sulfides, in the order Me < Et < *i*Pr < *t*Bu.

MK and NPA charges and Mulliken spin populations have been calculated for both the planar and the perpendicular forms to look at how they are influenced by the rotation around the $C_{Ar}-S$ bond. From the values collected in Chart 1 for the $PhSR^{\bullet+}$ series, it can be noted that in the planar form higher values of the Mulliken spin population are at the sulfur atom and that these values do not appreciably change with the nature of the alkyl group. A significant Mulliken spin population is also observed at the para position (larger than at the ortho positions), which is in line with the already mentioned importance of the resonance structure **1**. It appears therefore that the alkyl phenyl sulfide radical cations are sulfur-centered radical cations with some delocalization onto the ring occurring in the planar form. In agreement with this conclusion, the spin density at sulfur significantly increases as we pass to the perpendicular form.

In the para-substituted radical cations (Chart 2), a similar situation as that of $PhSR^{\bullet+}$ holds for $4\text{-}NCC_6H_4SMe^{\bullet+}$, which also appears to be a sulfur-centered radical cation with some Mulliken spin population delocalized at the nitrogen, in line with a significant role of the resonance structure **2**. In this case too, on going to the less stable perpendicular form, the spin density increases at sulfur and decreases at nitrogen.

A significant decrease in both MK charge and spin density at sulfur is, however, observed when the EDGs NMe_2 and OMe



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are the para ring substituents. Moreover in 4-$Me_2NC_6H_4SMe^{\bullet+}$ the spin density is slightly higher at nitrogen than at sulfur. Interestingly, as we move to the less stable perpendicular conformations a quite drastic decrease in charge and spin density (particularly the latter) at the sulfur atom occurs, which is exactly the opposite of what is observed with $PhSR^{\bullet+}$. The same phenomenon is observed when the charges are derived from the NPA, even though the absolute values are somewhat different (Chart 1S). Clearly, 4-$MeOC_6H_4SMe^{\bullet+}$ and 4-$Me_2NC_6H_4SMe^{\bullet+}$ have more aromatic radical cation character with some charge and spin density delocalized at the sulfur atom than sulfur-centered radical cation character. In other words, $PhSR^{\bullet+}$ and 4-$NCC_6H_4SMe^{\bullet+}$ are sulfur-centered radical cations with a phenyl substituent, whereas 4-$Me_2NC_6H_4SMe^{\bullet+}$ and 4-$MeOC_6H_4SMe^{\bullet+}$ (particularly the former one) are aromatic radical cations with a SMe group as substituent. Nevertheless, it is important to note that in both the dimethylamino- and methoxy-substituted systems the delocalization of charge and spin density at the sulfur atom is sufficient to make sulfur oxidation the dominant reaction in the one electron-transfer oxidations of 4-$Me_2NC_6H_4SMe$ and 4-$MeOC_6H_4SMe$.[29]

Finally, it is of interest to briefly discuss the calculated IE values for the alkyl phenyl sulfide series for both the planar and perpendicular conformations. A regular decrease in the calculated values for both forms is observed in the order Me > Et > *i*Pr > *t*Bu. In the case of the planar forms, this order reflects the greater importance of the steric effects of the alkyl group in the neutral sulfide than in the radical cation where, as already seen, steric effects are largely offset by the conjugative effects. Because steric effects should play no role in the perpendicular form, the observed trend might be due to some stabilization of the charge on sulfur by the electron-releasing effect of the alkyl group, which in the gas phase should decrease in the order *t*Bu > *i*Pr > Et > Me.[30]

When the calculated IE values are compared with the experimental ones (which come from PES experiments and are therefore vertical IEs), a good agreement is observed for the perpendicular conformations, especially considering that calculated IE usually underestimate the experimental value.[31]

In the case of the planar conformations, the experimental values do not show the clear trend observed in our calculations, even though some of the experimental values determined for thioanisole are higher than those reported for PhSEt and PhS*i*Pr, which are similar to one another. Unfortunately, no experimental value is available for the planar form of PhS*t*Bu because this sulfide is almost completely in the perpendicular conformation.

Finally, in Table 1 are also reported the oxidation potentials for PhSR in MeCN and it is interesting to note that these values increase in the order Me < Et < *i*Pr < *t*Bu, which is the opposite of that found for the calculated IEs. A possible explanation is that of a steric inhibition of solvation of the alkyl sulfide radical cation, whose importance should increase with the steric requirements of the alkyl group, i.e., in the order Me < Et < *i*Pr < *t*Bu. Because, as already discussed, $PhSMe^{\bullet+}$ are mainly sulfur-centered radical cations, the solvation of the positive charge on sulfur can be very sensitive to the bulkiness of the S-bonded alkyl group.

Conclusions

DFT calculations have shown that the most stable conformation for the radical cations of alkyl phenyl sulfides (alkyl = Me, Et, *i*Pr, *t*Bu) and of some para-substituted thioanisoles is the planar one, confirming previous conclusions based on ESR experiments. The rotational barriers have also been calculated for the first time and are quite high, from 12.307 to 19.496 kcal/mol. In the $PhSR^{\bullet+}$ series the barrier decreases in the order Me > Et > *i*Pr > *t*Bu, in line with the increasing steric strain in the planar conformer. Clearly, in the radical cation the very strong conjugation of the sulfur atom with the aromatic π system is the most important factor determining the preferred conformation. The reverse is observed instead with the neutral alkyl phenyl sulfides, whereas in the aryl-substituted thioanisoles the steric and the electronic effects seem to have a much similar role.

The analysis of MK charges and spin densities revealed that $PhSR^{\bullet+}$ and 4-$NCC_6H_4SR^{\bullet+}$ are mainly sulfur-centered radical cations with some charge and spin delocalization at the aromatic ring (mostly at the para position), whereas 4-$Me_2NC_6H_4SMe^{\bullet+}$ and 4-$MeOC_6H_4SMe^{\bullet+}$ are essentially aromatic radical cations with some charge and spin density at the sulfur atom.

A regular decrease has been observed in the calculated IE values for the alkyl phenyl series in the order Me > Et > *i*Pr > *t*Bu, which, in the case of the planar form, has been attributed to the greater importance of the steric effects in the neutral sulfide rather than in the radical cation. The analogous trend for the perpendicular form should be, instead, due to the different capacity of the alkyl group to stabilize the charge on the sulfur atom. The comparison between the calculated data and the experimental ones, whenever the latter are available, showed that the agreement is generally very good, thus confirming the reliability of the DFT predicting power.

Acknowledgment. The Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR) and the University "La Sapienza" are acknowledged for their financial support.

Supporting Information Available: Total energies, angles, and bond lengths of the optimized planar and perpendicular conformers for PhSR (Tables 1S−4S), ArSMe (Tables 5S−7S), $PhSR^{\bullet+}$ (Tables 8S−11S), $ArSMe^{\bullet+}$ (Tables 12S−14S), isotropic Fermi contact couplings for $ArSR^{\bullet+}$ (Table 15S), charges derived from the NPA for planar and perpendicular $ArSR^{\bullet+}$ (Chart 1S). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) The conformational equilibrium of 4-MeOC$_6$H$_4$SMe was studied for 0° ≤ ϕ ≤ 180°, and it was found that the cis and trans isomers have a similar energy.

(21) This value is, as expected, in good agreement with that found by Bobrowski et al.[8] using a smaller basis set.

(22) The conformational equilibrium of 4-MeOC$_6$H$_4$SMe$^{\bullet+}$ was studied for 0° ≤ ϕ ≤ 180°, and it was found that the trans isomer has an energy a little lower than that of the cis isomer.

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