Effect of Ring Substitution on the S−H Bond Dissociation Enthalpies of Thiophenols. An Experimental and Computational Study

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There are conflicting reports on the origin of the effect of Y substituents on the S−H bond dissociation enthalpies (BDEs) in 4-Y-substituted thiophenols, 4-YC_6H_4S−H. The differences in S−H BDEs, [4-YC_6H_4S−H] − [C_6H_5S−H], are known as the total (de)stabilization enthalpies, TSEs, where TSE = RSE − MSE, i.e., the radical (de)stabilization enthalpy minus the molecule (de)stabilization enthalpy. The effects of 4-Y substituents on the S−H BDEs in thiophenols and on the S−C BDEs in phenyl thioethers are expected to be almost identical. Some S−C TSEs were therefore derived from the rates of homolyses of a few 4-Y-substituted phenyl benzyl sulfides, 4-YC_6H_4S−$CH_2C_6H_5$, in the hydrogen donor solvent 9,10-dihydroanthracene. These TSEs were found to be −3.6 ± 0.5 (Y = NH_2), −1.8 ± 0.5 (CH_3O), 0 (H), and 0.7 ± 0.5 (CN) kcal mol^{-1}. The MSEs of 4-$YC_6H_4SCH_2C_6H_5$ have also been derived from the results of combustion calorimetry, Calvet-drop calorimetry, and computational chemistry (B3LYP/6-311+G(d,p)). The MSEs of these thioethers were −0.6 ± 1.1 (NH_2), −0.4 ± 1.1 (CH_3O), 0 (H), −0.3 ± 1.3 (CN), and −0.8 ± 1.5 ($COCH_3$) kcal mol^{-1}. Although all the enthalpic data are rather small, it is concluded that the TSEs in 4-YC_6H_4SH are largely governed by the RSEs, a somewhat surprising conclusion in view of the experimental fact that the unpaired electron in $C_6H_5S^\bullet$ is mainly localized on the S. The TSEs, RSEs, and MSEs have also been computed for a much larger series of 4-YC_6H_4SH and 4-$YC_6H_4SCH_3$ compounds by using a B3P86 methology and have further confirmed that the S−H/S−CH_3 TSEs are dominated by the RSEs. Good linear correlations were obtained for TSE = $\rho^+\sigma_p^+(Y)$, with ρ^+ (kcal mol^{-1}) = 3.5 (S−H) and 3.9 (S−CH_3). It is also concluded that the SH substituent is a rather strong electron donor with a σ_p^+(SH) of −0.60, and that the literature value of −0.03 is in error. In addition, the SH rotational barriers in 4-YC_6H_4SH have been computed and it has been found that for strong electron donating (ED) Ys, such as NH_2, the lowest energy conformer has the S−H bond oriented perpendicular to the aromatic ring plane. In this orientation the SH becomes an electron withdrawing (EW) group. Thus, although the OH group in phenols is always in-plane and ED irrespective of the nature of the 4-Y substituent, in thiophenols the SH switches from being an ED group with EW and weak ED 4-Ys, to being an EW group for strong ED 4-Ys.

Recently, some of us wrote an account describing the variations in the X−H bond dissociation enthalpies, BDE, for 4-substituted toluenes, anilines, and phenols, 4-YC_6H_4XH, in terms of the electronic properties of Y, XH, and X$^\bullet$, eq 1.[1] The interaction of Y as an electron donating (ED) or as an electron withdrawing (EW) substituent with XH in the molecule and with X$^\bullet$ in the radical are *both* responsible for the observed changes in the X−H BDEs. These interactions are responsible for (de)stabilizing 4-YC_6H_4XH relative to C_6H_5XH and (de)stabilizing 4-$YC_6H_4X^\bullet$ relative to $C_6H_5X^\bullet$. The associated enthalpic changes can be quantified by means of isodesmic reactions, eqs 2−4. The molecular stabilization enthalpy (MSE) is defined by eq 2, and the radical stabilization enthalpy (RSE) is given by eq 3. The total stabilization enthalpy (TSE) is given by eq 4, and the TSE (=RSE − MSE) reflects the relative change in the X−H BDE within a family of 4-YC_6H_4XH compounds.

$$\text{4-}YC_6H_4XH \longrightarrow \text{4-}YC_6H_4X^\bullet + H^\bullet \qquad (1)$$

$$C_6H_5XH + C_6H_5Y \xrightarrow{\text{MSE}} \text{4-}YC_6H_4XH + C_6H_6 \qquad (2)$$

$$C_6H_5X^\bullet + C_6H_5Y \xrightarrow{\text{RSE}} \text{4-}YC_6H_4X^\bullet + C_6H_6 \qquad (3)$$

$$C_6H_5X^\bullet + \text{4-}YC_6H_4XH \xrightarrow{\text{TSE}} \text{4-}YC_6H_4X^\bullet + C_6H_5XH \qquad (4)$$

The XH groups, NH_2 and OH, are EDs, and when they are present in a molecule together with an EW Y group, there is a stabilization of 4-YC_6H_4XH relative to C_6H_5XH, i.e., $\Delta H_2 <$

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0. On the other hand, in the corresponding anilinyl and phenoxyl radicals, the $N^{\bullet}$ and $O^{\bullet}$ moieties are EWs, and when they are present in combination with an EW Y group, there is a destabilization of 4-$YC_6H_4X^{\bullet}$ relative to $C_6H_5X^{\bullet}$, i.e., $\Delta H_3 > 0$. These different MSE/RSE effects lead to *linear* Hammett type relationships between the 4-$YC_6H_4X{-}H$ TSEs and the substituent constants $\sigma_p^+(Y)$ for both ED and EW Ys, i.e., TSE $= \rho^+\sigma_p^+(Y)$. The importance of such empirical relationships is evident and, provided that $\sigma^+(Y)$ for meta and ortho positions are known, they can be used to predict the TSEs in polysubstituted anilines and phenols with an accuracy of about 1−2 kcal mol^{-1}. The relative kinetics for hydrogen atom transfer processes are, of course, strongly related to TSEs and therefore the aforementioned equation can also be used to describe the relative H-atom donor reactivities for families of 4-YC_6H_4XH compounds.

The separation of the MSE or RSE (the fundamental components) from the TSE (which can be determined by various experimental methods, see below) is not straightforward. The MSE could be calculated by using the experimental enthalpies of formation of the species involved. However, these data are frequently not sufficiently reliable to be very useful and often they are simply not available. Therefore, theoretical calculations have been used to deconvolute the TSE into its two components. For anilines about 60% of the TSE originates from the RSE, whereas for phenols the RSE contribution has increased to about 74%.[2] The rationale for this difference is that NH_2 is a stronger π-ED than OH, while $N^{\bullet}$ is a weaker EW moiety than $O^{\bullet}$. Experimental and theoretical studies on the TSEs for anilines and for phenols have been shown to yield compatible results almost irrespective of the level of theory.[2]

In our account we also briefly discussed the S−H TSEs in 4-substituted thiophenols.[1] According to computational studies[3] a linear relationship is obeyed between the S−H TSE and $\sigma_p^+(Y)$, suggesting a behavior similar to that found for the anilines and phenols.[1] Moreover, these computations indicated that the S−H TSE is almost entirely governed (about 90%) by the RSE.[3a,b] That is, the interaction of Y in the radical, 4-$YC_6H_4S^{\bullet}$, eq 3, completely dominates its interaction in the molecule, 4-YC_6H_4SH. If this were actually true, the free electron on $S^{\bullet}$ would be expected to be strongly delocalized into the aromatic ring. However, ESR spectroscopic studies indicate that there is roughly 2.5 times as much spin density on sulfur in 2,4,6-tri-*tert*-butylphenylthiyl as on oxygen in 2,4,6-tri-*tert*-butylphenoxyl.[4a] Moreover, strong delocalization of the unpaired electron in $C_6H_5S^{\bullet}$ would cause the $C{-}S^{\bullet}$ bond to have substantial double bond character (as is the case in the $C_6H_5O^{\bullet}$[4b]). On the contrary, a Raman spectroscopic study has revealed that the C−S bond in $C_6H_5S^{\bullet}$ is essentially a single bond,[4c] implying that the free electron resides almost exclusively on the sulfur atom. Consequently, there would appear to be little or no additional enthalpic (de)stabilization of the 4-$YC_6H_4S^{\bullet}$ radical relative $C_6H_4S^{\bullet}$ by means of an electronic interaction of the unpaired electron with Y. On the other hand, however, a photoelectron (PE) spectroscopic study on C_6H_5SH has shown that there is a strong donating interaction between the lone pairs in the 3p orbital of sulfur and the π-system of the aromatic ring, suggesting that the SH acts as an ED group.[5] This implies that a (de)stabilization of 4-YC_6H_4SH relative to C_6H_5SH (the MSE) would be a relatively more important component of the S−H TSE than the RSE, a conclusion that is contradicted by the computational results.[3a,b] Adding to the confusion are the σ_p^+ values for sulfur-containing groups. The experimental σ_p^+ of the SH group is close to zero (−0.03),[6,7a] which strongly suggests that there is hardly any relative (de)stabilization in 4-YC_6H_4SH. Conversely, the value of σ_p^+ of the SCH_3 group is −0.60,[6,7b] indicating that, in contrast with SH, the SCH_3 group is a fairly strong ED. For comparison, the σ_p^+s for the ED groups, OH and OCH_3, are about equal in magnitude ($\sigma_p^+ = -0.78$),[8] and it seems reasonable to assume that this should also hold for SH and SCH_3.

TABLE 1: Experimental[a] and Computed S−H TSEs (kcal mol^{-1}) in 4-Y-Thiophenols at 298 K

Y	σ_p^{+} [b]	EC[c]	EC[d]	ETE[e]	PAC[f]	B3LYP[g]	MP2[h]
NH_2	−1.30		−9.3	−6.9		−5.4[i]	−2.4[i]
CH_3O	−0.78	−1.2	−2.2	−2.5	−2.0	−3.6	−2.3
CH_3	−0.31	−0.7	−0.8	−0.9	−0.5	−2.0	−0.8
H	0	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
Cl	0.11	−0.1	0.1		0.9	−1.5	−0.4
Br	0.15	1.7	0.2	−0.4			
CF_3	0.61				0.7	1.8	1.3
CN	0.66					1.9	1.1
NO_2	0.79	3.1	2.3			3.0	2.0

[a] Experimental methods: electrochemical cycle (EC), electron-transfer equilibration (ETE), photoacoustic calorimetry (PAC). [b] From ref 6. [c] From ref 9a, solvent sulfolane. $C_6H_5S{-}H$ BDE = 78.7 kcal mol^{-1} (at 1 bar, see ref 10). [d] From ref 9b, solvent DMSO, $C_6H_5S{-}H$ BDE = 79.5 kcal mol^{-1} (at 1 bar, see ref 10). [e] From ref 9c, solvent water, $C_6H_5S{-}H$ BDE = 80.4 kcal mol^{-1} (at 1 bar, calculated according to the guidelines presented in ref 11a and with $\Delta S(C_6H_5SH) - \Delta S(C_6H_5S^{\bullet}) = 4$ cal mol^{-1} K^{-1} from ref 11b, see also ref 10). [f] From ref 9d, solvent 0.4 M di-*tert*-butyl peroxide in benzene, $C_6H_5S{-}H$ BDE = 83.9 kcal mol^{-1} (at 1 bar, see ref 10). [g] From ref 3a, (RO)B3LYP/6-311++G(2df,2p)//B3LYP/6-311G(d,p), $C_6H_5S{-}H$ BDE = 79.5 kcal mol^{-1}. [h] From ref 3b, ROMP2/6-311++G(d,p), $C_6H_5S{-}H$ BDE = 75.5 kcal mol^{-1}. [i] In the lowest enthalpy conformer, the SH is orientated perpendicular to the plane of the phenyl ring.

Experimentally, the S−H TSEs in 4-YC_6H_4SH have been investigated by two electrochemical cycle (EC) methods,[9a,b] an electron-transfer equilibration (ETE) method[9c] and a photoacoustic calorimetric (PAC) technique.[9d] These results, together with the computational TSEs, are presented in Table 1. It can be noted from this table that for Y = NH_2 the data show a large variation, with the difference between the experimental and the computed (MP2) TSEs being as large as 7 kcal mol^{-1} (which is well beyond any expected experimental or computational uncertainty).

Given the foregoing inconsistencies regarding the fundamental behavior of SH and $S^{\bullet}$ in sulfur-substituted aromatic systems, we have embarked on a systematic study in an effort to unravel the MSE and RSE contributions to the 4-YC_6H_4SH TSEs. As one part of this effort, the S−C BDEs (TSEs) have been determined for some 4-Y-substituted phenyl benzyl sulfides by their homolysis in the presence of 9,10-dihydroanthracene as a radical scavenger. Previously, we have demonstrated that such an approach with 4-Y-substituted phenyl benzyl ethers gave O−C TSEs identical with the O−H TSEs for 4-Y-substituted phenols and with the O−C TSEs for 4-Y-substituted anisoles.[8] The MSEs for some of the 4-Y-substituted phenyl benzyl sulfides have also been obtained by determining their enthalpies of formation, using combustion calorimetry and Calvet drop microcalorimetry. Finally, high-level computations have been applied to derive the energetics and the geometric parameters for a large series of 4-$YC_6H_4SH(CH_3)$ compounds and the corresponding phenylthiyl radicals.

Results

Thermolysis of 4-Y-Phenyl Benzyl Sulfides. The rates of thermolysis of the four 4-Y-phenyl benzyl sulfides, 4-Y-PBS (Y = NH_2, CH_3O, H, and CN), have been determined in 9,10-dihydroanthracene, AnH_2, at a reaction temperature of 548 K

TABLE 2: Typical Product Distribution (in %) for the Thermolysis of $4\text{-}YC_6H_4SCH_2C_6H_5$ in 9,10-Dihydroanthracene[a]

Y	T/K	$10^{-5}t$/s	C_6H_5-CH_3	4-Y-C_6H_4SH	$4\text{-}YC_6H_4S$-$CH_2C_6H_5$	$2\text{-}SH\text{-}5\text{-}YC_6H_3$-$CH_2C_6H_5$
NH_2	523	1.5	32.7	32.4	63.1	4.2
CH_3O	548	1.1	40.4	40.9	55.8	3.8
H	548	6.0	30.9	30.1	59.4	9.7[b]
CN	548	6.7	23.6	21.8	69.4	4.9

[a] See also Tables S1−S4 of the Supporting Information; T = reaction temperature, t = reaction time; e.g., 6×10^5 s for Y = H; the product distribution is calculated by using $[4\text{-}YC_6H_4SCH_2C_6H_5]_{t=0} = [4\text{-}YC_6H_4SCH_2C_6H_5]_{t=t} + [C_6H_5CH_3]_{t=t} + [2\text{-}SH\text{-}5\text{-}YC_6H_3CH_2C_6H_5]_{t=t}$. [b] Sum of $2\text{-}SHC_6H_4CH_2C_6H_5$ and $4\text{-}SHC_6H_4CH_2C_6H_5$, the 2-/4-product ratio is 7.2.

for Y = CH_3O, H, and CN and at 523 K for Y = NH_2. After S−C cleavage, eq 5, the thiophenoxyl and the benzyl radicals that have escaped from the solvent cage, i.e., that have become “free”, eq 6, are scavenged by AnH_2 (eqs 8 and 9) and form the corresponding thiophenol[12] and toluene. Disproportionation of the 9,10-dihydroanthracenyl radicals yields anthracene, An, and AnH_2 (eq 10).

$$4\text{-}YC_6H_4SCH_2C_6H_5 \rightleftharpoons [4\text{-}YC_6H_4S^\bullet\ {}^\bullet CH_2C_6H_5]_{cage} \quad (5)$$

$$[4\text{-}YC_6H_4S^\bullet\ {}^\bullet CH_2C_6H_5]_{cage} \rightarrow 4\text{-}YC_6H_4S^\bullet + {}^\bullet CH_2C_6H_5 \quad (6)$$

$$[4\text{-}YC_6H_4S^\bullet\ {}^\bullet CH_2C_6H_5]_{cage} \rightarrow 2\text{-}SH\text{-}5\text{-}YC_6H_3CH_2C_6H_5 \quad (7)$$

$$4\text{-}YC_6H_4S^\bullet + AnH_2 \rightarrow 4\text{-}YC_6H_4SH + AnH^\bullet \quad (8)$$

$$C_6H_5CH_2^\bullet + AnH_2 \rightarrow C_6H_5CH_3 + AnH^\bullet \quad (9)$$

$$AnH^\bullet + AnH^\bullet \rightarrow An + AnH_2 \quad (10)$$

The thermolysis of $4\text{-}YC_6H_4SCH_2C_6H_5$ also yields an in-cage, radical−radical combination (isomerization) product, $2\text{-}SH\text{-}5\text{-}YC_6H_3CH_2C_6H_5$, eq 7 (in the case of Y = H a second isomeric product is found as well, which we have identified as $4\text{-}SHC_6H_4CH_2C_6H_5$). The identities of the isomers for Y = NH_2, CH_3O, H, and CN are based on their recorded mass spectra which show in all cases the M − 78 ion as the most abundant species. Under comparable reaction conditions, a similar isomerization has been observed during the thermolysis of the analogues 4-substituted-phenyl benzyl ethers with 2-hydroxydiphenylmethane derivatives being among the products.[13] The thermolysis of phenyl benzyl ether gives an isomerization yield of 20%[13a] or 10−15%[13c] for the sum of 2- and 4-hydroxydiphenylmethane, whereas for 4-Y-phenyl benzyl ethers the yield is about 17%, independent of Y.[13b] In Table 2 typical product distributions are presented for the thermolyses of the various $4\text{-}YC_6H_4SCH_2C_6H_5$. The yields of the isomerization product(s) as a percentage of the total products are 11% (NH_2), 9% (OCH_3), 24% (H), and 17% (CN), yields that are comparable with those found in the 4-substituted-phenyl benzyl ether studies.[13a,b] Experiments with Y = $CH_3C(O)$ were unsuccessful due to the competitive hydrogenation by AnH_2 of the carbonyl moiety in $4\text{-}CH_3C(O)C_6H_4SCH_2C_6H_5$.[14]

The overall first-order rate constants, k_{ov}, for Y = NH_2, CH_3O, H, and CN have been obtained from plots of $\ln([4\text{-}YC_6H_4SCH_2C_6H_5]_{t=t}/[4\text{-}YC_6H_4SCH_2C_6H_5]_{t=0})$ versus t, using an internal mass balance defined as $[4\text{-}YC_6H_4SCH_2C_6H_5]_{t=0} = [4\text{-}YC_6H_4SCH_2C_6H_5]_{t=t} + [C_6H_5CH_3]_{t=t} + [C_6H_5CH_3]_{t=t}/R$, where R is the average $[C_6H_5CH_3]_{t=t}/[2\text{-}SH\text{-}5\text{-}Y\text{-}C_6H_3SHCH_2C_6H_5]_{t=t}$ ratio within the series of experiments (see the Supporting Information). Reaction −5, the in-cage, radical−radical recombination that reforms $4\text{-}YC_6H_4SCH_2C_6H_5$, is expected to occur but is, of course, “invisible” in these experiments. The measurable rate constant for S−C bond cleavage is therefore given by $k_{ov} = k_6 + k_7$. All these linear plots yield slopes, k_{ov}, with correlation coefficients of >0.99. The activation enthalpies, E_{ov}, are calculated from the rate constants with use of a preexponential factor of $\log(A/s^{-1}) = 15.2$[8] (Table 3). The “invisible” back reaction may have caused k_{ov} to be slightly underestimated, which would lead to a slight overestimation (probably < ∼1 kcal mol^{-1}, see below) of $4\text{-}YC_6H_4S{-}CH_2C_6H_5$ BDEs. (This could also be true for our earlier thermolytic studies on $4\text{-}YC_6H_4OCH_2C_6H_5$.)[8] Fortunately, this (hypothetical) invisible reaction is likely to be of very similar, and minor, importance for all the phenyl benzyl sulfides and, therefore, it will not affect our conclusions about the differences in S−C BDEs produced by the different Y substituents.

TABLE 3: First-Order Rate Constants for S−C Homolysis, k_{ov} ($=k_6 + k_7$), in 4-Y−Phenyl Benzyl Sulfides and for O−C Homolysis, k_{11}, in 4-Y-Phenyl Benzyl Ethers in 9,10-Dihydroanthracene

Y	T/K	$10^7k_{ov}/s^{-1}$	E_{ov}[a]	S−C TSE[b]	$10^7k_{11}/s^{-1}$ [c]	$E_{a,11}$[a]
NH_2	523	30.5	49.7	−3.6		
CH_3O	548	51.4	51.4	−1.8	1700	47.6
H	548	9.5	53.2	0.0	10.7	53.1
CN (CF_3)[d]	548	4.9	53.9	0.7	0.54	56.3

[a] Calculated from k_{ov} or k_{11} and with $\log(A/s^{-1}) = 15.2$ and the E_a values(in kcal mol^{-1}). [b] S−C TSE (kcal mol^{-1}) = E_{ov}(4-Y) − E_{ov}(4-H). The estimated error in the TSE is 0.5 kcal mol^{-1}. [c] From ref 8, the rate constants for 4-CF_3 and 4-CH_3O have been recalculated to 548 K from the original data by using $\log(A/s^{-1}) = 15.2$. In Table 2 of ref 8, the reported rate constants for 4-CF_3- and 4-H-phenyl benzyl ether had been inadvertently interchanged. [d] In the 4-Y-phenyl benzyl ether study Y is CF_3.

The S−C BDE in Phenyl Benzyl Sulfide. Previously, we have reported on the rates of O−C bond homolyses for 4-Y-substituted phenyl benzyl ethers, eq 11, using the same experimental procedure (see Table 3).[8] In that study it was

$$4\text{-}YC_6H_4OCH_2C_6H_5 \rightarrow 4\text{-}YC_6H_4O^\bullet + {}^\bullet CH_2C_6H_5 \quad (11)$$

shown that the rate constant measured at one temperature for O−C homolysis of, e.g., phenyl benzyl ether, when combined with a preexponential factor of $\log(A_{11}/s^{-1}) = 15.2$, gave an enthalpy of activation of 53.1 kcal mol^{-1}. Assuming that $E_{a,11} = \Delta H_{11}$, the O−C BDE at 298 K becomes 53.1 + 0.4 = 53.5 kcal mol^{-1} at the thermodynamic standard state of 1 bar.[10] According to this procedure, a S−C BDE of 53.6 kcal mol^{-1} at 298 K is calculated for phenyl benzyl sulfide.

The S−C and the O−C BDEs found by thermolyses of the benzyl thioethers and benzyl ethers in solution can be validated by comparison with the very low-pressure pyrolyses (VLPP) studies on thioanisole[15] and on anisole.[8] The VLPP method is known to provide accurate gas-phase BDEs. Under VLPP conditions, only S−C cleavage, eq 12, or O−C cleavage, eq 13, takes place. The related kinetic parameters are presented in Table 4.

$$C_6H_5SCH_3 \rightarrow C_6H_5S^\bullet + CH_3^\bullet \quad (12)$$

$$C_6H_5OCH_3 \rightarrow C_6H_5O^\bullet + CH_3^\bullet \quad (13)$$

It is obvious from Table 4 that the rates of bond homolysis for thioanisole and anisole are (almost) identical over a wide

TABLE 4: Kinetic and Thermodynamic Data (kcal mol^{-1}) for Homolysis of Thioanisole (S−C)[15] and Anisole (O−C)[8]

	T range	E_a	$\log(A/s^{-1})$	T_m (K)	BDE[a]
$C_6H_5S-CH_3$	945−1250	63.6	15.3	1100	66.7
$C_6H_5O-CH_3$	900−1100	63.9	15.3	1000	65.7

[a] According to eq 14, with $\Delta\bar{C}_{p,m}$ (in cal mol^{-1} K^{-1}) of 0.30 (1000 K) for $C_6H_5OCH_3$, and −1.11 (1100 K) for $C_6H_5SCH_3$, computed at the B3LYP/6-31G(d,p)// B3LYP/6-31G(d,p) level of theory (this work). For comparison, $\Delta\bar{C}_{p,m}$ for eq 12 has previously been estimated to be −2.1 cal mol^{-1} K^{-1}.[15]

range of temperature. This means that the rate constants for S−C and O−C bond cleavage for phenyl benzyl sulfide and phenyl benzyl ether, respectively, at one temperature are expected to be about equal, which is in full accordance with our experimental results in the liquid phase (see Table 3). The E_as in Table 4 can be converted into BDEs at 298 K by use of eq 14.[10] In this equation, T_m is the average temperature of the experiment

$$\mathrm{BDE} = E_a + RT_m - \Delta\bar{C}_{p,m}(T_m - 298) \tag{14}$$

and $\Delta\bar{C}_{p,m}$ is the average change in the molar heat capacity between T_m and 298 K, as obtained from B3LYP computations. Hence, eq 14 yields a S−CH_3 BDE of 66.7 ± 0.5 kcal mol^{-1} for thioanisole, and an O−CH_3 BDE of 65.7 ± 0.5 kcal mol^{-1} for anisole, both values being at the standard state of 1 bar and 298 K. When the increment of −12.5 kcal mol^{-1} between the C−C BDEs in $C_6H_5CH_2-CH_3$ and CH_3-CH_3[16] is applied to the S−CH_3 BDE in thioanisole, the S−C BDE in phenyl benzyl sulfide is predicted to be 54.2 kcal mol^{-1}. This predicted value is in outstanding agreement with our experimental value of 53.6 kcal mol^{-1} (see above) which, therefore, appears not to have been overestimated. In the same way, an O−C BDE in phenyl benzyl ether of 65.7−12.5 = 53.2 kcal mol^{-1} is derived that is also in outstanding agreement with the experimental value of 53.1 kcal mol^{-1} and also has not been overestimated.

It is also of interest to note that the X−H BDEs in C_6H_5XH are clearly different, 80.1[17] and 86.7[10] kcal mol^{-1} for X = S and O, respectively, whereas the X−C BDEs in phenyl benzyl sulfide and phenyl benzyl ether or in thioanisole and anisole are almost identical. We suggest that this is due to steric repulsion between the benzyl or methyl groups and the ortho hydrogen atoms in the ethers with a consequent weakening of their O−C bonds relative to the O−H bond in phenol and that such steric interactions are relatively unimportant in the two thioethers because S−C bonds are longer than O−C bonds.

Enthalpies of Formation of 4-Y-Phenyl Benzyl Sulfides [Y = H, CH_3O, CN, NH_2, C(O)CH_3], 4-Y-PBS, from Calorimetric Experiments and Computational Chemistry Calculations. The standard molar enthalpies of combustion of 4-Y-PBS (Y = H, CH_3O, CN) at 298.15 K obtained in this work are shown in Table 5 (see the Supporting Information for details). These results refer to reactions 15−17 and lead to the corresponding enthalpies of formation in the crystalline state (Table 5) by using $\Delta_f H^o_m(CO_2, g) = -(94.051 \pm 0.031)$ kcal mol^{-1},[19] $\Delta_f H^o_m(H_2O, l) = -(68.315 \pm 0.010)$ kcal mol^{-1},[19] and $\Delta_f H^o_m(H_2SO_4{\cdot}115H_2O, l) = -(212.199 \pm 0.095)$ kcal mol^{-1}.[20]

$$C_{13}H_{12}S(cr) + 17.5O_2(g) + 110H_2O(l) = 13CO_2(g) + H_2SO_4{\cdot}115H_2O(l) \tag{15}$$

$$C_{14}H_{14}OS(cr) + 18.5O_2(g) + 109H_2O(l) = 14CO_2(g) + H_2SO_4{\cdot}115H_2O(l) \tag{16}$$

$$C_{14}H_{11}NS(cr) + 18.25O_2(g) + 110.5H_2O(l) = 14CO_2(g) + 0.5N_2(g) + H_2SO_4{\cdot}115H_2O(l) \tag{17}$$

Also listed in Table 5 are the enthalpies of sublimation of 4-H-PBS, 4-CH_3O-PBS, and 4-CN-PBS at 298.15 K as obtained by Calvet drop microcalorimetry. For 4-H-PBS and 4-CN-PBS, the experimental measurements gave $\Delta_{sub}H^o_m$(4-H-PBS) = 23.38 ± 0.33 kcal mol^{-1} at 310.9 K and $\Delta_{sub}H^o_m$(4-CN-PBS) = 27.77 ± 0.50 kcal mol^{-1} at 350.7 K. Correction of these results to 298.15 K by using eq 18, where $C^o_{p,m}$(cr) and $C^o_{p,m}$(g) represent the molar heat capacities of the compounds in the solid

$$\Delta_{sub}H^o_m(298.15\ \mathrm{K}) = \Delta_{sub}H^o_m(T) + [C^o_{p,m}(g) - C^o_{p,m}(cr)](298.15 - T) \tag{18}$$

and gaseous states, gives the results listed in Table 5. In the case of 4-CH_3O-PBS, the enthalpy of the calorimetric process (cr, 298.15 K) → (g, 350.7 K) was determined to be 28.67 ± 0.65 kcal mol^{-1}. The corresponding isothermal enthalpy of sublimation at 298.15 K indicated in Table 5 was derived from this value and the $C^o_{p,m}(g)dT$ term integrated over the interval 350.7−298.15 K. The heat capacity data used in these corrections were obtained as follows: $C^o_{p,m}$(4-H-PBS, cr) = 61.02 cal K^{-1} mol^{-1} was measured in this work by Calvet drop calorimetry in the temperature range 298.15−310.9 K, $C^o_{p,m}$(4-CN-PBS, cr) = 63.74 cal K^{-1} mol^{-1} was estimated by Kopp's method;[21] $C^o_{p,m}$(4-H-PBS, g) = 50.38 cal K^{-1} mol^{-1} and $C^o_{p,m}$(4-CN-PBS, g) = 56.50 cal K^{-1} mol^{-1} at 298.15 K, and $C^o_{p,m}$(4-CH_3O-PBS, g) = $0.18377T + 4.96949$ cal K^{-1} mol^{-1} were derived from DFT calculations at the B3LYP/6-31G(d) level of theory with frequencies scaled by 0.9614.[22]

From the $\Delta_f H^o_m$(cr) and $\Delta_{sub}H^o_m$ data in Table 5 it was possible to obtain the enthalpies of formation of gaseous 4-H-PBS, 4-CN-PBS, and 4-CH_3O-PBS that are also listed in Table 5. The corresponding experimental values for 4-NH_2-PBS and 4-C(O)CH_3-PBS could not be determined due to decomposition of the samples during vaporization or incomplete combustion (see Experimental Section). They were, therefore, estimated by calculations of the enthalpy of the isodesmic and isogyric reactions, eq 19.

$$C_6H_5SCH_2C_6H_5(g) + C_6H_5Y(g) \rightarrow 4\text{-}YC_6H_4SCH_2C_6H_5(g) + C_6H_6(g) \tag{19}$$

At the B3LYP/6-311+G(d,p) level of theory, the following reaction enthalpies were obtained: −0.38 (Y = CH_3O), −0.53 (Y = CN), −0.65 (Y = NH_2), and −0.79 kcal mol^{-1} (Y = C(O)CH_3). These values, together with the enthalpy of formation of gaseous benzyl phenyl sulfide obtained in this work and the $\Delta_f H^o_m$(g) data for C_6H_6, $C_6H_5OCH_3$, C_6H_5CN, $C_6H_5NH_2$, and $C_6H_5C(O)CH_3$ included in Table 5,[10,18,23,24] led to the $\Delta_f H^o_m$(g) data listed under the heading B3LYP/6-311+G(d,p). The calculated values of $\Delta_f H^o_m$(g) for 4-CN-PBS and 4-CH_3O-PBS are in good agreement with the corresponding experimental results indicating a very good consistency between the theoretical and the experimental standard enthalpies of formation. The DFT $\Delta_f H^o_m$(g) results for 4-NH_2-PBS and 4-C(O)CH_3-PBS should therefore be reliable.

When comparing the *relative* enthalpies of formation (Table 5, numbers in parentheses in the last two columns) of 4-YC_6H_4-$SCH_2C_6H_5$ and C_6H_5Y it is clear that the effect of substitution is nearly the same for both series of compounds.

TABLE 5: Standard Molar Enthalpies (kcal mol^{-1}) of Combustion, Formation, and Sublimation of 4-Y-Phenyl Benzyl Sulfides and Related Compounds at 298.15 K[a]

	4-$YC_6H_4SCH_2C_6H_5$					C_6H_5Y
Y	$-\Delta_c H^o_m$	$\Delta_f H^o_m$(cr)	$\Delta_{sub} H^o_m$	$\Delta_f H^o_m$(g)	$\Delta_f H^o_m$(g) B3LYP/6-311+G(d,p)	$\Delta_f H^o_m$(g)
H	1800.253 ± 0.614	23.80 ± 0.74	23.52 ± 0.33	47.32 ± 0.81 (0.0)		19.82 ± 0.12[b]
CH_3O	1921.929 ± 0.729	−16.87 ± 0.86	26.89 ± 0.65	10.02 ± 1.08 (37.3)	8.79 ± 0.72 (38.5)	−18.33 ± 0.22[c,d] (38.2)
CN	1887.863 ± 0.638	51.53 ± 0.79	28.15 ± 0.50	79.68 ± 0.93 (−32.4)	79.47 ± 0.92 (−32.2)	52.3 ± 0.5[b] (−32.5)
NH_2					47.67 ± 0.74 (−0.3)	20.82 ± 0.26[e] (−1.0)
$C(O)CH_3$					17.94 ± 1.12 (29.4)	−8.77 ± 0.67[e] (28.6)

[a] In parentheses, the differences in $\Delta_f H^o_m$(g) relative to $\Delta_f H^o_m$(4-H-PBS, g); in the case of the B3LYP/6-311+G(d,p) results (obtained from the computed ΔH_{19} in conjunction with the experimental heats of formation) the differences refer to the experimental $\Delta_f H^o_m$(4-H-PBS, g). [b] Reference 23. [c] Reference 18. [d] Reference 10. [e] Reference 24.

TABLE 6: B3P86-Computed MSEs and RSEs (kcal mol^{-1}) Differences in 4-Y-Substituted Thiophenols and Thioanisoles at 298 K

		S−H			$S-CH_3$		
	σ_p^{+}[a]	MSE	RSE	TSE	MSE	RSE	TSE
$N(CH_3)_2$[b]	−1.70	−0.76	−6.65	−5.89	−0.34	−6.65	−6.31
NH_2[b]	−1.30	−0.91	−5.91	−5.00	−0.54	−5.91	−5.37
OCH_3[b]	−0.78	−0.54	−3.78	−3.23	−0.19	−3.78	−3.59
SCH_3	−0.60	0.21	−3.18	−3.38	0.44	−3.18	−3.61
SH	−0.60[c]	0.31	−2.27	−2.59	0.21	−2.27	−2.48
CH_3	−0.31	0.21	−1.07	−1.28	0.25	−1.07	−1.32
H[d,e]	0	0	0	0	0	0	0
Cl	0.11	0.35	−0.12	−0.47	0.12	−0.12	−0.24
Br	0.15	0.33	−0.06	−0.39	0.05	−0.06	−0.10
CF_3	0.61	−0.25	1.47	1.72	−0.64	1.47	2.11
CN	0.66	−0.43	1.45	1.88	−1.02	1.45	2.46
NO_2	0.79	−0.65	2.23	2.88	−1.33	2.23	3.55

[a] From ref 6 unless otherwise noted. [b] The lowest energy conformers with Y = $N(CH_3)_2$, NH_2, and OCH_3 have the S−H and $S-CH_3$ bonds perpendicular to the aromatic plane (see Figure 1). [c] See text. [d] The B3P86 calculated C_6H_5S-H BDE is 79.8 kcal mol^{-1} (exptl 80.1, see ref 17) and the calculated $C_6H_5S-CH_3$ BDE is 63.6 (exptl 66.7, see Table 4). According to B3P86 (ref 25a), the C_6H_5O-H BDE is 87.8 kcal mol^{-1} (exptl 86.7, see ref 10) and the $C_6H_5O-CH_3$ BDE is 62.9 kcal mol^{-1} (exptl 65.7, see Table 4). The CBS-QB3 calculated BDEs are 81.1 (C_6H_5S-H), 68.1 ($C_6H_5S-CH_3$), 87.1 (C_6H_5O-H, ref 10), and 65.7 kcal mol^{-1} ($C_6H_5O-CH_3$, ref 10). This means that the enthalpic change for the reaction $C_6H_5SCH_3 + C_6H_5OH \rightarrow C_6H_5SH + C_6H_5OCH_3$ is 8.7 (B3P86) or 8.4 kcal mol^{-1} (CBS-QB3), both values being in reasonable agreement with the experimental value of 7.6 kcal mol^{-1}. [e] At the UCCSD(T) level, the calculated C_6H_5S-H BDE is 77.6 kcal mol^{-1} (exptl 80.1, see ref 17) and the TSEs are −2.5 (NH_2), −1.0 (CH_3), −0.2 (Cl), and 2.0 (NO_2).

The $\Delta_f H^o_m$(g) for phenyl benzyl sulfide can also be estimated by two independent thermodynamic procedures. First, the increment in $\Delta_f H^o_m$(g) upon replacing a CH_2 by S in the couples $CH_3CH_2CH_3/CH_3SCH_3$ (16.1) and $C_6H_5C_2H_5/C_6H_5SCH_3$ (16.1) can be used, in conjunction with the $\Delta_f H^o_m$(g) for bibenzyl of 34.2 kcal mol^{-1},[18] to calculate a $\Delta_f H^o_m$(g) for phenyl benzyl sulfide of 34.2 + 16.1 = 50.2 kcal mol^{-1}. Second, a BDE(S−C) of 53.6 kcal mol^{-1} at 298 K was found for phenyl benzyl sulfide from our kinetic experiments (see above). Taking the enthalpies of formation of the benzyl radical and the phenylthiyl radical to be 49.7[16] and 54.9 kcal mol^{-1},[17] respectively, yields a $\Delta_f H^o_m$(g) for phenyl benzyl sulfide of 49.7 + 54.9 − 53.6 = 51.0 kcal mol^{-1} in good agreement with the 50.2 kcal mol^{-1} found by the first procedure. However, the experimental value for $\Delta_f H^o_m$(g) of 47.3 kcal mol^{-1} is about 3−4 kcal mol^{-1} lower than these estimated values. At present, we have no explanation for these discrepancies.

Computed MSEs, RSEs, and TSEs for the Cleavage of S−H/S−CH_3 Bonds in Thiophenols and Thioanisoles. The MSE, RSE, and TSE data for a series of 4-$YC_6H_4S-H(CH_3)$ compounds have been computed by using the B3P86/6-311G(2d,2p)//B3P86/6-31G(d)[25a] methodology that has previously been shown to predict accurate BDEs for a test set of 62 bonds including O−H, O−C, S−H, and S−C bonds.[25a] To simplify the computations, the S−C TSEs in 4-$YC_6H_4SCH_2C_6H_5$ were modeled by the S−C TSEs in 4-$YC_6H_4SCH_3$. This procedure was previously demonstrated to yield virtually identical O−C TSEs for the oxygen analogues, 4-$YC_6H_4OCH_3$ and 4-$YC_6H_4OCH_2C_6H_5$.[8] These results are presented in Table 6. The UCCSD(T)/6-31++(d,p)//B3P86/6-31G(d) methodology with its smaller basis set was also employed[25b] (see footnote *e* in Table 6). With B3P86, the S−H BDE in thiophenol is well reproduced, 79.8 (theory) and 80.1[17] (experiment) kcal mol^{-1}, but the calculated $C_6H_5S-CH_3$ BDE is about 3 kcal mol^{-1} lower than the experimental value (63.6 vs 66.7 kcal mol^{-1}). Recently we have shown that the CBS-QB3 chemistry model accurately calculates the O−H BDE in phenol and the O−C BDE in anisole.[10] With CBS-QB3 the C_6H_5S-H and the $C_6H_5S-CH_3$ BDEs are calculated to be 81.1 and 68.1 kcal mol^{-1}, respectively. Both BDEs are (slightly) overestimated by CBS-QB3, in accordance with results from our earlier work using this method.[10] (With the UCCSD(T) method, the S−H BDE is underestimated by 3.5 kcal mol^{-1}.)

The differences between the B3P86 MSEs for 4-YC_6H_4SH and 4-$YC_6H_4SCH_3$ range from 0.2 for Y = Cl to 0.6 kcal mol^{-1} for Y = NO_2. The trends in the MSEs for 4-YC_6H_4SH and 4-$YC_6H_4SCH_3$ are quite similar, suggesting that the electronic interactions of SH and SCH_3 with Y in thiophenols and thioanisoles are about the same. Furthermore, as Table 6 shows, the differences between the TSEs for Y = SH and SCH_3 are much smaller than would have been anticipated from the large difference in the tabulated σ_p^+ values for these two substituents, viz., −0.03 and −0.60, respectively (see the Introduction). We propose that it is the literature σ_p^+(SH) value that is in error. We expect its true value to be close to, or identical with, that for SCH_3 and therefore use a value for σ_p^+(SH) = −0.60 henceforth (see Table 6).

It is clear from Table 6 that the TSEs are dominated by the (de)stabilization of the 4-Y-substituted phenylthiyl radical (i.e., by the RSEs). Furthermore, there is a change in the lowest energy conformation of 4-YC_6H_4SH when Y is a strong π-electron donor such as CH_3O or NH_2 (see footnote *b*, Table 6). One consequence of the perpendicular orientations of the S−H and S−CH_3 bonds is that the MSEs for these compounds are negative. Thus, 4-YC_6H_4SH having a strong ED Y or a strong EW Y are relatively lower in energy than C_6H_5SH! This is very different from the situations for 4-YC_6H_4OH and 4-$YC_6H_4NH_2$ for which the MSEs with ED Ys are always positive (destabilization of the molecule), without a conformational change of the OH or the NH_2 group. For example, the

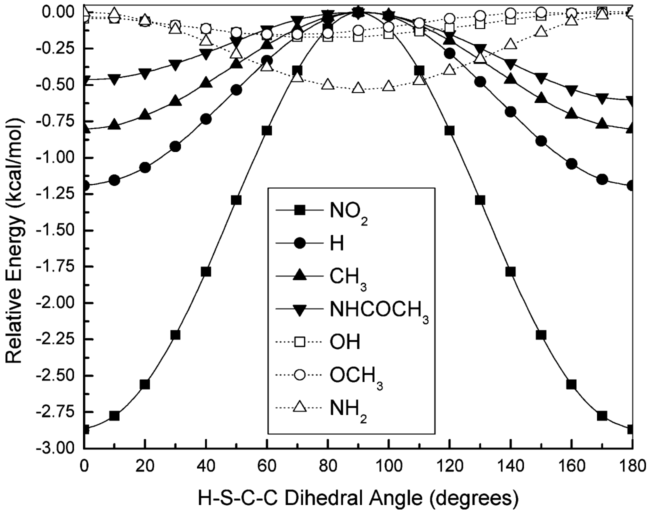

Figure 1. B3P86/6-311++G(3df,3pd)-computed rotational energy barriers for the SH group in 4-YC_6H_4SH.

MSE with Y = $N(CH_3)_2$ for 4-YC_6H_4OH is 2.0 kcal mol^{-1} and it is 1.8 kcal mol^{-1} for 4-$YC_6H_4NH_2$.[2] Hence, an important parameter for MSE considerations is the effect of the conformation of the lowest energy conformer and therefore the rotational barrier height, E_{rot}, for XH in C_6H_5XH. Experimentally, the E_{rot}s in C_6H_5XH have been determined as 5.73 (X = NH),[26a] 3.47 (X = O),[26b] and 0.76 (X = S)[26c] kcal mol^{-1} for the rotation of XH (from the in-plane to the perpendicular position). These values can be considered to be a rough measure of the lone pair conjugative interaction energy for the in-plane conformer with the π system of the aromatic ring. However, it would be wrong to assume that disrupting this resonance by a 90° rotation of XH would change XH from a π-electron donating group into a σ-electron withdrawing group, because the two lone pairs on X still have some overlap with the aromatic π electrons. This has been experimentally demonstrated for XH = OH where it has been shown that the measured rate constants for hydroxylic hydrogen atom abstraction from 4-CH_3O-2,3,5,6-$(CH_3)_4C_6OH$ and from 2,3,4,5,6-$(CH_3)_5C_6OH$ by alkylperoxyl radicals are about the same.[27] Since rates of reaction of phenols with alkylperoxyl radicals depend on the O−H BDEs, and since these correlate well with $\sum\sigma^+$ of the Ys, it means that although the CH_3O group in 4-CH_3O-2,3,5,6-$(CH_3)_4C_6OH$ is forced into a position perpendicular to the plane of aromatic ring,[28] it still acts as a moderately strong electron donor with an effective σ^+ substituent constant close to the −0.31 of a 4-CH_3 group.

To examine the effect of rotation in 4-YC_6H_4SH further, we have computed the rotational barriers for the SH group in 4-YC_6H_4SH (with Y = NH_2, OCH_3, OH, CH_3, H, $NHCOCH_3$, and NO_2) at the B3P86 level. These results are displayed in Figure 1. Two different global lowest energy conformers can be discerned for 4-YC_6H_4SH: a conformer in which the S−H bond is coplanar with the aromatic ring (dihedral angle φ(HSCC) = 0°) and a perpendicular conformer with φ = 90°. For Y = NO_2, H, CH_3, and $NHCOCH_3$, the lowest energy conformers have the S−H bond aligned in the phenyl ring plan. However, for Y = NH_2 the preferred conformer has the S−H bond perpendicular to the ring plane and with Y = OH and OCH_3 the perpendicular conformers are very slightly favored. Even in C_6H_5SH the SH group is essentially a free rotor with an experimental E_{rot} = 0.76 kcal mol^{-1}.[26c] (A completely free rotor would have E_{rot} equal to or smaller than kT, i.e., 0.59 kcal mol^{-1} at 298 K.[29]) It has been proposed that the effective conformation for $C_6H_5SCH_3$ in the gas phase is the average between the in-plane and the perpendicular conformers, i.e., φ = 45°, whereas in solution a φ = 23° has been advanced.[30] Free rotation means that the effective conformation of C_6H_5SH (and $C_6H_5SCH_3$) will depend on temperature and the surrounding medium (solvent). The rotational barriers have been determined by NMR studies in CCl_4 at 305 K for various 4-YC_6H_4SH: E_{rot} = 2.2 (NO_2), 0.93 (Br), 0.76 (H), 0.45 (CH_3), −0.45 (OCH_3), and −0.8 (NH_2) kcal mol^{-1}.[26c] These values are in qualitative agreement with the present computations. Thus, the average orientation of the SH group depends on Y, ranging from almost coplanar, φ = 0° for Y = NO_2, to φ > 45° for Y = OCH_3 and NH_2. Consequently, for π-ED Ys in 4-YC_6H_4SH the SH is out of plane, and according to the MSE calculations it now acts as an EW group ($\sigma_p^+ > 0$, a result that contrasts with the electronic effect of a perpendicular OCH_3 group, see above). Conversely, for π-electron acceptor Ys, the lowest energy conformer has the S−H bond in the aromatic plane where it acts as an π-ED ($\sigma_p^+ < 0$).

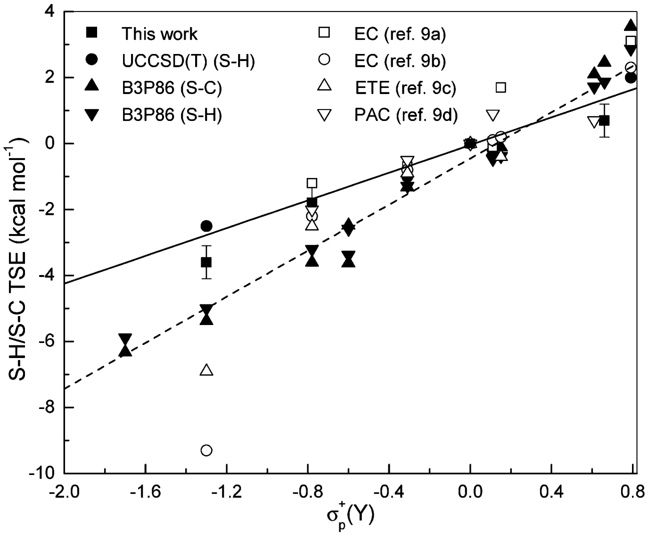

Figure 2. Plots of the experimental 4-$YC_6H_4S{-}H$ TSEs (Table 1) and 4-$YC_6H_4S{-}CH_2C_6H_5$ TSEs (Table 3) and the computed 4-$YC_6H_4S{-}H$ and 4-$YC_6H_4S{-}CH_3$ TSEs (Table 6, see also footnote *e*) vs σ_p^+(Y) (in kcal mol^{-1}). The regression lines have been drawn with the computed S−H TSEs: B3P86 (dashed) and UCCSD(T) (solid).

Discussion

Substituent Effects on 4-$YC_6H_4S{-}H$ BDEs. It seems reasonable to assume that the experimental S−C TSEs for the 4-Y-phenyl benzyl sulfides presented in Table 3 will be (almost) identical with the S−H TSEs for 4-YC_6H_4SH. In Figure 2 the experimental (Table 3) and computational TSEs (Table 6) from the present work and all the experimental data from the literature (Table 1) have been combined and plotted according to TSE = $\rho^+\sigma_p^+$(Y).

This figure shows that the experimental data points for Y = NH_2 with TSEs, viz. −9.3[9b] and −6.9[9c] kcal mol^{-1}, are at odds with the value of −3.6 kcal mol^{-1} derived from the present experimental study. It has been suggested that the low TSEs found in the electrochemical cycle (EC) and electron-transfer equilibration (ETE) studies result from a change in the energy of the intermolecular hydrogen bond between the NH_2 group and the solvent and that this influences the measured free energy change of the electron-transfer reactions.[3b] Figure 2 shows some additional scatter of the experimental S−H TSEs, but this scatter is within the error limits of the different methods. The slopes, ρ^+, for the two computational methods used in this study are

TABLE 7: Calculated ρ^+ Values from the Linear Equation TSE = $\rho^+\sigma_p^+$(Y) for the S−H/S−C TSEs in $4\text{-YC}_6\text{H}_4\text{SH(CH}_2\text{X)}$[a]

ρ^+	bond	no.	R^2	method	ref
2.83	S−H	6	0.834	EC	9a
2.80	S−H	6	0.991	EC	9b[b]
2.54	S−H	4	0.899	ETE	9c[b]
1.87	S−H	4	0.936	PAC	9d[c]
3.87	S−H	8	0.959	B3LYP	3a
2.13	S−H	8	0.944	MP2	3b
2.15	S−C	4	0.940	thermolysis	Table 3
3.49	S−H	12	0.977	B3P86	Table 6[d]
2.19	S−H	4	0.955	UCCSD(T)	Table 6[e]
3.94	S−C	12	0.977	B3P86	Table 6[d]
1.80	S−C	6		equilibrium	31 [f]

[a] In kcal mol^{-1}; X = H or C_6H_5. no.: number of 4-Y compounds investigated, including Y = H. R^2: linear regression coefficient. Methods: see also footnotes *a*, *g*, and *h* of Table 1. [b] Excluding the data for Y = NH_2 from the EC and ETE studies. [c] Excluding the data for Y = Cl from the PAC study since the absorbance of the $4\text{-ClC}_6\text{H}_4\text{SH}$ may well have convoluted the result. [d] With σ_p^+(SH) = −0.60. [e] See footnote *e* of Table 6. [f] See text.

markedly different with UCCSD(T), despite its smaller basis set, giving a better fit to experiment than B3P86 (or B3LYP). The ρ^+ values from each of the experimental and computational studies are compiled in Table 7.

Ito et al.[31] have studied the reversible addition of some 4-Y-substituted thiophenoxyl radicals to olefins, eq 20:

$$4\text{-YC}_6\text{H}_4\text{S}^\bullet + \text{CH}_2{=}\text{CHR} \rightleftharpoons 4\text{-YC}_6\text{H}_4\text{SCH}_2\text{C}(^\bullet)\text{HR} \quad (20)$$

from which $4\text{-YC}_6\text{H}_4\text{S}$−C TSEs can also be derived. The decay rates of $4\text{-YC}_6\text{H}_4\text{S}^\bullet$ were determined in the presence of sufficient oxygen to scavenge the carbon-centered radicals generated, thus preventing the reverse reaction. From the kinetic data, the equilibrium constants, K_{20}, were calculated. A Hammett plot of log K_{20} vs σ_p^+(Y) (Y = CH_3O, CH_3, *tert*-butyl, H, Cl, and Br) for R = naphthyl gave a ρ^+ of 1.36 or 1.36 × 2.303RT = 1.8 kcal mol^{-1}. With methyl methacrylate as the olefin and with Y = CH_3O, CH_3, H, and Cl, an identical ρ^+ value was found. Provided ΔS_{20} is, as expected, independent of the nature of Y, the TSEs for phenyl alkyl sulfides can be represented as TSE = $\rho^+\sigma_p^+$ (Y) = 1.8σ_p^+(Y), in reasonable agreement with our experimental ρ^+ and the UCCSD(T)-computed ρ^+.

For phenols (and anilines) the orientation of the hydroxyl (and NH_2) group is the same for ED and EW Ys and a single linear relationship exists between the O−H (and NH−H) TSEs and σ_p^+(Y) for $4\text{-YC}_6\text{H}_4\text{OH}$ (and $4\text{-YC}_6\text{H}_4\text{NH}_2$) for both ED and EW Ys.[1,2] However, the orientation of the S−H bond in $4\text{-YC}_6\text{H}_4\text{SH}$ has been found to depend on whether Y is ED or EW (see Figure 1). This raises the question as to whether the single linear relationship between σ_p^+(Y) and the S−H (and S−C) TSEs that is observed for both ED and EW Ys is “reasonable”. In this connection, it is instructive to compare the computed electronic interactions in thioanisole and anisole.[30] The two lone pairs on sulfur are nonequivalent and the two lone pairs on oxygen are also nonequivalent. According to the Natural Bond Orbital method, one lone pair on sulfur has an almost pure p-character and conjugates with the aromatic ring in the S−H bond in-plane conformer. The second lone pair on sulfur has about 70% s-character and is much lower in energy than the p-type lone pair (for comparison the second lone pair on oxygen has only about 40% s-character).[30] When the SCH_3 group in $C_6H_5SCH_3$ is perpendicular to the aromatic ring the charge on the ring carbon atoms (ortho/para) changes from negative to positive, whereas when the OCH_3 group in C_6H_5-OCH_3 is in the perpendicular position, the charges on these carbon atoms remain negative.[30] The enthalpic (macroscopic) effect is that by changing the orientation of the SH group in $4\text{-YC}_6\text{H}_4\text{SH}$ from coplanar to perpendicular the repulsive interaction with an ED Y can be diminished. The consequence is that the MSEs for thiophenols are largely attenuated in comparison with the MSEs for phenols, e.g., the calculated differences in the MSEs between Y = NH_2 and NO_2 are 0.26 ($4\text{-YC}_6\text{H}_4\text{SH}$, Table 6) and 3.4 ($4\text{-YC}_6\text{H}_4\text{OH}$)[2] kcal mol^{-1}. As can be seen from Table 6, the TSEs and the RSEs for each of the substituted thiophenols are almost identical, underscoring the unimportance of molecule (de)stabilizing enthalpic effects. Additional calculations on the spin density and the charge on sulfur in the $4\text{-YC}_6\text{H}_4\text{S}^\bullet$ show the change in charge on sulfur correlates extremely well with TSE/RSE (and σ_p^+(Y)) for both ED and EW Ys.[32,33] Hence, polar effects in the substituted phenylthiyl radicals dominate the TSEs and therefore a linear relationship between the S−H TSE and the σ_p^+(Y) for $4\text{-YC}_6\text{H}_4$-SH including ED and EW Ys is completely “reasonable”.

The MSE/RSE/TSE Distribution in Thiophenols. To this point, our analysis of the MSEs/RSEs has been based exclusively on theoretical calculations. The experimental TSEs for 4-Y-phenyl benzyl sulfides are −3.6 ± 0.5 (NH_2), −1.8 ± 0.5 (CH_3O), 0 (H), and 0.7 ± 0.5 (CN) kcal mol^{-1} (Table 3), and the MSEs are −0.6 ± 1.1 (NH_2), −0.4 ± 1.1 (CH_3O), 0 (H), and −0.3 ± 1.3 (CN) kcal mol^{-1} obtained from results of combustion calorimetry, Calvet-drop calorimetry, and computational chemistry (B3LYP/6-311+G(d,p)). Hence, the contributions of the RSEs to the TSEs, i.e., TSE = RSE − MSE, are calculated to be −4.2 ± 1.2 (NH_2), −2.2 ± 1.2 (CH_3O), 0 (H), and 0.4 ± 1.4 (CN) kcal mol^{-1}. The RSEs obtained by B3P86 computations (see Table 6) of −5.9 (NH_2), −3.8 (CH_3O), 0 (H), and 1.4 (CN) kcal mol^{-1} for $4\text{-YC}_6\text{H}_4\text{S}^\bullet$ radicals differ somewhat from the experimentally derived RSEs. Most DFT methods are unable to properly describe highly delocalized species[25a] and although eq 3 takes advantage of the cancellation of computational errors, some deviation between theory and experiment remains. However, all these enthalpies are rather small, and the inherent inaccuracies of the experimental and computational methods do not allow a decision as to where the errors lie. In conclusion, this study has shown that substituent effects on the S−H BDEs in $4\text{-YC}_6\text{H}_4\text{SH}$ are, indeed, governed mainly by the (de)stabilization of the $4\text{-YC}_6\text{H}_4\text{S}^\bullet$ radicals.

Experimental Section

Methods. *Thermolysis of 4-Y-Phenyl Benzyl Sulfides.* The decomposition of 4-Y-phenyl benzyl sulfides (4-Y-PBS) was studied in 9,10-dihydroanthrancene, AnH_2, as the hydrogen-donating solvent. For each 4-Y-PBS at least five ampules (ca. 2 mL in volume) were filled with ca. 500 mg of AnH_2 and about 20 mg of 4-Y-PBS. The ampules were sealed after degassing with use of three cool−pump−heat cycles and were then placed in a temperature-controlled GC oven. They were removed at known times, cooled to room temperature, then opened, and their content was dissolved in 6 mL of CH_2Cl_2 and finally 10 μL anisole was added as an external standard. The products of the thermolysis experiments were identified by GC/MS (at 70 eV) with use of MS library spectra[18] and quantified by GC/FID (average of two injections). GC molar response factors were determined by using authentic samples or by standard estimation procedures.

Combustion Calorimetry. The standard enthalpies of combustion of the 4-Y-PBS (Y = H, CH_3O, CN) compounds were measured with the isoperibol rotating-bomb combustion calorimeter previously described.[34] The bomb was tantalum lined and had an internal volume of 329 cm^3. The sample in pellet form was placed in a platinum crucible and burned under 3.04 MPa of oxygen, with 15 cm^3 of water inside the bomb. The duration of the fore, main, and after periods was ca. 20 min each. Discharge of a 1400 μF capacitor through a platinum wire connecting the two electrodes ignited the cotton thread fuse and subsequently the sample. Calorimetric temperatures were measured to 1×10^{-4} K with a quartz thermometer (Hewlett-Packard HP 2804) interfaced to a microcomputer programmed to compute the adiabatic temperature change. For each experiment the ignition temperature was chosen so that the final temperature would be close to 298.15 K. The rotation of the bomb was started when the temperature rise of the main period reached about 0.63 of its total value, and was continued throughout the experiment. It has been shown that by adopting this procedure, the frictional work due to the rotation of the bomb is automatically accounted for in the calculation of the adiabatic temperature rise.[35] The HNO_3 formed was analyzed by the Devarda's alloy method.[36] The energy equivalent of the calorimeter, $\epsilon° = (20369.0 \pm 2.3)$ J K^{-1}, was determined in the conventional way without bomb rotation[37] from the combustion of benzoic acid (NIST SRM 39j) whose standard massic energy of combustion under certificate conditions was $\Delta_c u(BA)_{cert} = -(26434 \pm 3)$ J g^{-1}.[38] The enthalpy of combustion of 4-C(O)CH_3-PBS could not be measured due to incomplete combustion of the sample.

Calvet Drop Calorimetry. The enthalpies of sublimation of 4-Y-PBS (Y = H, CH_3O, CN) were measured by using the electrically calibrated Calvet drop-sublimation microcalorimeter previously described.[39] The samples with masses in the ranges 1.5−4.9 (4-H-PBS), 7.8−15.1 (4-CH_3O-PBS), and 1.9−4.5 mg (4-CN-PBS) were weighed to 1×10^{-6} g inside a small glass capillary and dropped into the calorimetric cell, under a N_2 atmosphere, from inside a furnace placed above the entrance of the cell. The temperature of the furnace was 298 K and the duration of the equilibration time before dropping the sample ca. 20 min. The temperature of the calorimetric cell was set at 340.15 (4-H-PBS), 388.15 (4-CH_3O-PBS), and 388.15 K (4-CN-PBS). An endothermic peak due to the heating of the sample from room temperature to the temperature of the calorimeter was first observed (in the case of 4-CH_3O-PBS this included fusion). After the signal returned to the baseline the sample and reference cells were simultaneously evacuated and the measuring curve corresponding to the evaporation of the sample was acquired. Several attempts were made to determine $\Delta_{vap}H^o_m$ for 4-NH_2-PBS. However, a dark red, viscous liquid residue was always found inside the calorimetric cell at the end of the experiments, therefore the results where discarded.

Theoretical Calculations. The calculations of the isodesmic reactions 19 and of the standard molar heat capacities of 4-H-PBS, 4-CH_3O-PBS, and 4-CN-PBS in the gaseous state reported in this study have been carried out with the Gaussian-98 package.[40] The geometries were fully optimized and the energies were calculated by using the Becke's three-parameter hybrid method[41] with the Lee, Yang, and Parr LYP [42] correlation functional (B3LYP), employing the 6-31G(d)[43] and 6-311+G-(d,p) basis sets.[44] The obtained electronic energies, zero-point vibrational energies, and thermal corrections used to derive the enthalpies at 298.15 K are given as the Supporting Information.

For the BDE calculations, the B3P86/6-311G(2d,2p)//B3P86/6-31G(d) model,[41,45] as implemented in Gaussian-03,[46] was used. Additional BDE calculations were performed with UCCSD(T)/6-311++G(d,p) as implemented in the Molpro package.[47] Rotational energy surfaces were generated [46] by performing relaxed scans of the H−S−C−C dihedral at the B3P86/6-311++G(3df,3pd) level.

Materials. Commercially available materials were used as received.

4-Aminophenyl Benzyl Sulfide. (a) Synthesis of 4-nitrophenyl benzyl sulfide: Potassium hydroxide (2.25 g, 40 mmol) was completely dissolved in 30 mL of ethanol (95%) at room temperature. Benzyl thiol (4.70 mL, 40 mmol) was then added in one portion with a syringe, followed by the addition of a solution of acetonitrile (100 mL) and 1-bromo-4-nitrobenzene (8.08 g, 40 mmol). The resulting reaction mixture was heated to reflux for 15 h, the solution turned from orange to red, and a yellow precipitate was formed on the inside wall of the flask. The reaction progress was monitored by GC/MS. Upon completion, the solvents were removed by evaporation, and the yellow solid was recrystallized from dichloromethane/hexanes at −20 °C to afford 9.6 g (98% yield) of pure product as yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H 4.28 (s, 2H), 7.31−7.43 (m, 7H), 8.10−8.14 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ_C 37.43, 124.34, 127.03, 128.22, 129.13, 129.26, 135.86, 145.63, 147.67.

(b) Synthesis of 4-aminophenyl benzyl sulfide: 4-Nitrophenyl benzyl sulfide (5.0 g, 20.4 mmol) was dissolved in 150 mL of ethyl acetate, and 10% Pd/C (1.25 g) was added in one portion. The reaction mixture was hydrogenated at atmospheric pressure for 36 h at room temperature. The reaction progress was monitored by GC/MS. The reaction mixture was filtered through a bed of Celite, and the filtrate was concentrated to give the crude product as a colorless liquid. The crude product was purified by column chromatography (hexane: ethyl acetate = 3:1) to achieve 100% purity (3.8 g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H 3.71 (br, s, 2H), 3.97 (s, 2H), 6.57−6.61 (m, 2H), 7.14−7.30 (m, 7H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ_C 42.19, 115.84, 123.35, 127.26, 128.70, 129.34, 135.16, 138.86, 146.63. HRMS calcd for $C_{13}H_{14}NS$ (M + 1) 216.0769, found 216.0735.

4-Methoxyphenyl Benzyl Sulfide. (a) Preparation of CsF-Celite: To a stirred suspension of 10 g of Celite 521 in 300 mL of distilled water was added 10.0 g of cesium fluoride (0.66 mol). The mixture was heated and stirred at 65 °C for 3 h, and the water was removed by rotary evaporation. The solid residue was taken up in 50 mL of acetonitrile and stirred for 1 h at room temperature, filtered, washed with acetonitrile, and dried under high vacuum for 48 h to give 19.8 g of CsF-Celite.

(b) Synthesis of 4-methoxyphenyl benzyl sulfide: CsF-Celite (3.42 g) was added to a solution of 4-methoxythiophenol (5.0 mL, 40.6 mmol) in 50 mL of acetonitrile at room temperature. To the vigorously stirred suspension was added benzyl bromide (7.2 mL, 60.9 mmol) dropwise with a syringe. The reaction mixture was then heated to reflux for 15 h. The progress of the reaction was monitored by GC/MS. After completion, 50 mL of ethyl acetate was added to the reaction mixture, which was then stirred for 30 min at room temperature. The Celite was filtered off and the filtrate was concentrated to give the crude product as a mixture of liquid (excess benzyl bromide) and orange solid. The crude product was purified by column chromatography (hexane:ethyl acetate = 5:1) followed by recrystallization from dichloromethane/hexanes at −20 °C; 6.8 g (73% yield) of pure product was obtained as white flakes. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H 3.81 (s, 3H), 4.01 (s, 2H), 6.81−6.83 (m, 2H), 7.21−7.31 (m, 7H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ_C 41.64, 55.71, 114.83, 126.48, 127.38, 128.77,

129.29, 134.49, 138.54, 159.62. HRMS calcd for $C_{14}H_{15}OS$ (M + 1) 231.0765, found 231.0791.

4-Acetylphenyl Benzyl Sulfide. Benzyl thiol (9.40 mL, 80 mmol) was dissolved in 40 mL of 95% ethanol, potassium hydroxide (4.49 g, 80 mmol) was added, and the resulting solution was heated to reflux until the KOH had completely dissolved. After the solution was cooled to room temperature, a solution of 4-fluoroacetophenone (9.71 mL, 80 mmol) in 40 mL of 95% ethanol was added dropwise by means of a syringe. The reaction mixture was then heated to reflux for 6 h and cooled to room temperature whereby a white precipitate was formed. The precipitate was filtered, washed with water, and recrystallized from ethyl acetate at −20 °C to afford 17.9 g (92% yield) of pure product as white needles. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H 2.58 (s, 3H), 4.24 (s, 2H), 7.29−7.41 (m, 7H), 7.85−7.87 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ_C 26.85, 37.61, 127.34, 127.94, 129.11, 129.15, 134.61, 136.66, 144.61, 197.59. HRMS calcd for $C_{15}H_{15}OS$ (M + 1) 243.0765, found 243.0880.

4-Cyanophenyl Benzyl Sulfide. To a solution of benzyl thiol (4.70 mL, 40 mmol) in 30 mL of ethanol (95%) was added potassium hydroxide (2.25 g, 40 mmol) at room temperature. This was stirred until the KOH was completely dissolved and a solution of 4-cyanobenzyl bromide (7.28 g, 40 mmol) in 50 mL of acetonitrile was added in one portion. The reaction mixture was heated to reflux for 30 h while the progress of the reaction was monitored by GC/MS. After completion of the reaction, the solvents were removed by rotary evaporation and the orange solid was purified by column chromatography (hexane:ethyl acetate = 5:1) followed by recrystallization from dichloromethane/hexanes at −20 °C. Yield 7.2 g (80% yield) of white fluffy needles. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ_H 4.23 (s, 2H), 7.29−7.40 (m, 7H), 7.51−7.53 (m, 2H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ_C 37.50, 108.99, 119.23, 127.75, 128.12, 129.12, 129.20, 132.63, 136.14, 144.89. HRMS calcd for $C_{14}H_{12}NS$ (M + 1) 226.0612, found 226.0695.

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Supporting Information Available: General analytical methods, ^{1}H and ^{13}C NMR spectra of the synthesized 4-Y-phenyl benzyl sulfides, additional product data for the decomposition of 4-Y-phenyl benzyl sulfides (Tables S1−S4), electronic energies, thermochemical corrections, and enthalpies of all species involved in reaction 19 (Table S5), and details of the combustion calorimetry experiments (procedures and results) (Tables S6−S8). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) (a) The S−H BDE in thiophenol is estimated to be 80.1 ± 0.5 kcal mol^{-1} (at 1 bar) on the basis of the S−C BDE in thioanisole, using the following equations: S−C BDE = $\Delta_f H(C_6H_5S^\bullet) + \Delta_f H(CH_3^\bullet) - \Delta_f H(C_6H_5SCH_3)$ leading to $\Delta_f H(C_6H_5S^\bullet) = 54.9$ kcal mol^{-1}, and S−H BDE = $\Delta_f H(C_6H_5S^\bullet) + \Delta_f H(H^\bullet) - \Delta_f H(C_6H_5SH)$ in combination with auxiliary thermodynamic quantities, see refs 15 and 18. A very recent computational paper employed CCSD(T) calculations and a dual extrapolation scheme to complete basis set with cc-pV*X*Z (*Z* = 2, 3) basis sets and reported a S−H BDE in thiophenol of 83.0 kcal mol^{-1} (ref 17b). This value is in good agreement with the value of 83.8 kcal mol^{-1} (at 1 bar, see ref 10) obtained by using PAC (ref 9d) but is at odds with all other experimental values (see footnotes to Table 1, and results given in the present work). Table 2 of ref 17b displays the computed S−H BDEs for a number of thiols using four computational methods. For thiophenol, the difference between the CCSD(T) S−H BDE and the BDE obtained by PAC is about 0.8 kcal mol^{-1}, while the other three computational methods gave differences ranging from 1.4 to 2.8 kcal mol^{-1}. In contrast, for H_2S and four alkanethiols all four computational methods gave results that do not differ from experiment by more than 0.9 kcal mol^{-1} and do not differ among themselves by more than 0.6 kcal mol^{-1}. This raises at least the possibility that CCSD(T) may perform poorly when electron delocalization can occur in a thiyl radical. Moreover, a $C_6H_5S\text{−}H$ BDE of 83.0 kcal mol^{-1} would increase $\Delta_f H(C_6H_5S^\bullet)$ to 57.8 kcal mol^{-1} and this would imply that the S−C BDEs in thioanisole and phenyl benzyl sulfide would increase by 2.9 kcal mol^{-1}. Such an increase would mean that the predicted rate constant for S−C bond homolysis of, e.g., phenyl benzyl sulfide at 548 K (see Table 3) would be about 14 times lower than that experimentally observed. This is well outside any experimental uncertainty, particularly because the expected "invisible" in-cage back reaction may well have caused this rate constant to be *underestimated*, see text. To fit the measured rate of this S−C homolysis to the higher $C_6H_5S\text{−}CH_2C_6H_5$ BDE would require an increase in log(*A*/s^{-1}) from 15.2 to an unreasonable 16.4. Therefore, because the thermokinetic data for the ethers (anisole and phenyl benzyl ether) and for the thioethers (thioanisole and phenyl benzyl sulfide) are internally consistent, we recommend (until further refinement is possible) a $C_6H_5S\text{−}H$ BDE of 80.1 ± 0.5 kcal mol^{-1}. (b) Cabral do Couto, P.; Costa Cabral, B. J.; Martinho Simões, J. A. *Chem. Phys. Lett.* **2006**, *421*, 504−507.

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(33) The charge on sulfur, q(S), in 4-YC$_6$H$_4$S$^\bullet$ decreases with ED Ys, i.e., the charge on sulfur becomes more negative, while with EW Ys the q(S) increases. The linear correlation of TSE with q(S) ($R^2 = 0.979$) also means that q(S) will correlate linearly with $\sigma_p{}^+$(Y). For the spin density, ρ(S), in 4-YC$_6$H$_4$S$^\bullet$ a positive linear correlation with the TSE is found with an R^2 of 0.883, the ρ(S) ranges from 0.64 (Y = NH$_2$) to 0.76 (Y = NO$_2$). These results suggest that with decreasing q(S) in 4-YC$_6$H$_4$S$^\bullet$, the spin density actually becomes less, i.e., the double bond character of the C−S bond increases. Moreover they show that in the phenylthiyl radical the spin is not localized exclusively on sulfur (see also ref 4b).

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