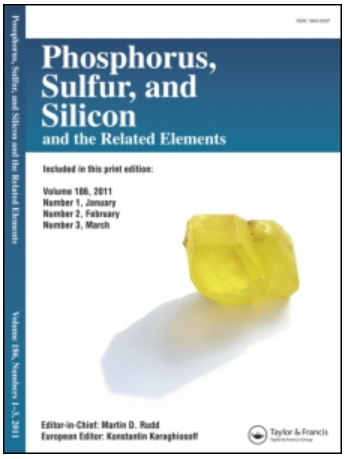

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Vessally, E.(2009) 'Theoretical Studies on *S*-Phenyl-thiabenzene, *S*-Phenyl-thianaphthalene, and *S*-Phenyl-thiaanthracene', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 10, 2636 — 2644
To link to this Article: DOI: 10.1080/10426500802539639
URL: http://dx.doi.org/10.1080/10426500802539639

Phosphorus, Sulfur, and Silicon, 184:2636–2644, 2009

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802539639

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Theoretical Studies on *S*-Phenyl-thiabenzene, *S*-Phenyl-thianaphthalene, and *S*-Phenyl-thiaanthracene

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The molecular structures of S-*phenyl-thiabenzene* ***1****,* S-*phenyl-1-thianaphthalene* ***2****,* S-*phenyl-2-thianaphthalene* ***3****, and* S-*phenyl-9-thiaanthracene* ***4*** *are studied by ab initio calculations using HF as well as DFT methods at the 6–311+G* level of theory. The non-planar boat conformers of* ***1–4*** *with 6π electrons in the heterocyclic ring appear to be more stable than the corresponding planar conformers with 8π electrons in the ring. The activation energy for the inversion at the sulfur atom is compared for* ***1–4****. Conformational flexibility of* ***1–4*** *is studied.*

Keywords Ab initio; aromatic character; DFT; HF; molecular structure; *S*-phenyl-9-thiaanthracene; *S*-phenyl-thiabenzene; *S*-phenyl-1-thianaphthalene; *S*-phenyl-2-thianaphthalene

INTRODUCTION

Thiabenzenes were first synthesized by Suld and Price 1961.[1] 1,2,4,6-Tetraphenylthiabenzene was prepared by the reaction of 2,4,6-triphenylthiopyrylium perchlorate with phenyl lithium under inert atmosphere. Thiabenzenes are of interest for chemists due to their rearrangement into thiopyrans.[2–10] Thiabenzenes are thermodynamically unstable; treatment with oxygen and hydrogen chloride gas yields oxypyrylium zwitterions.

1- and 2-thianaphthalenes and 9-thiaanthracene show similar properties with respect to those of thiabenzenes.[2] They are, however, more stable and more resistant to treatment with oxygen and hydrogen chloride gas.[2] Nevertheless, the studies of Senkler et al. contradict these properties.[11] Derivatives of thiabenzenes were synthesized, and the effects of electron-donating and -withdrawing groups were studied.[4–8] Moreover, aromaticity of a series of substituted six-membered λ^5-phosphorins has been evaluated.[12] As a continuation of our

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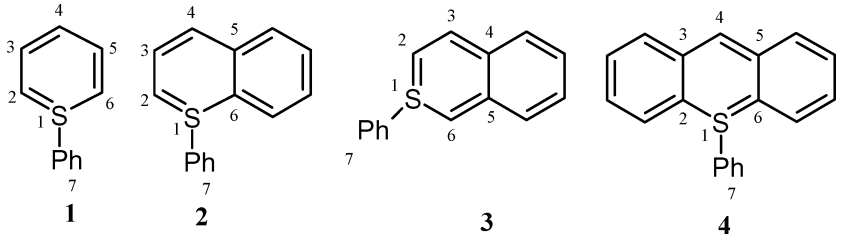


SCHEME 1 *S*-phenyl-thiabenzene **1**, *S*-phenyl-1-thianaphthalene **2**, *S*-phenyl-2-thianaphthalene **3**, and *S*-phenyl-9-thiaanthracene **4**.

studies,[13–15] we carried out ab initio calculations on thiabenzene and some related heterocycles.

EXPERIMENTAL

The molecular structures of **1–4**, shown in Scheme 1, were studied using ab initio methods. Geometry optimizations were carried out by HF and DFT methods (Figure 1).[16–18] A 6–311+G* basis set was used for all calculations. All calculations were performed using the Gaussian 98 program.[19] Global minima were specified on the corresponding energy surfaces through relax scan using Keyword "Freq".

RESULT AND DISCUSSION

Two canonical forms can be considered for sulfur as well as for phosphorus ylides and only one for nitrogen ylides. *S*-phenyl-thiabenzene **1**, *S*-phenyl-1-thianaphthalene **2**, *S*-phenyl-2-thianaphthalene **3**, and *S*-phenyl-9-thiaanthracene **4** have 6π electrons in the thiabenzene ring.

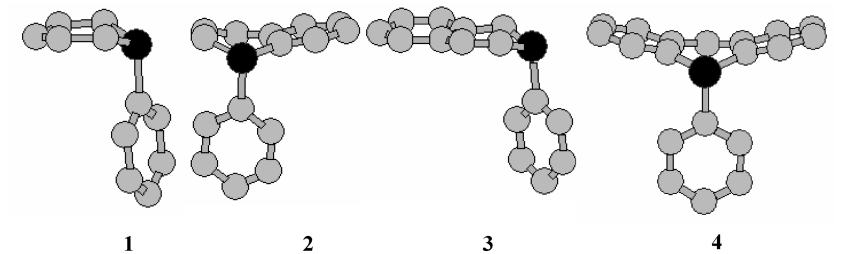


FIGURE 1 Optimized conformations of compounds **1–4**. Black balls represent the sulfur atom, gray balls the carbon atoms. The hydrogen atoms are not shown.

TABLE I Thermal Energies, Thermal Enthalpies, and Thermal Free Energies (kcal/mol) for the Optimized Conformations of 1–4

	HF			B3LYP		
	E	H	G	E	H	G
1	−514169.727	−514168.6073	−514224.48	−516388.325	−516387.2054	−516445.7
2	−609899.375	−609898.2554	−609960.19	−612743.943	−612742.8236	−612806.95
3	−609897.247	−609896.1278	−609958.2	−612741.365	−612740.2459	−612804.69
4	−705624.152	−705623.0316	−705692.61	−709095.749	−709094.6296	−709165.72

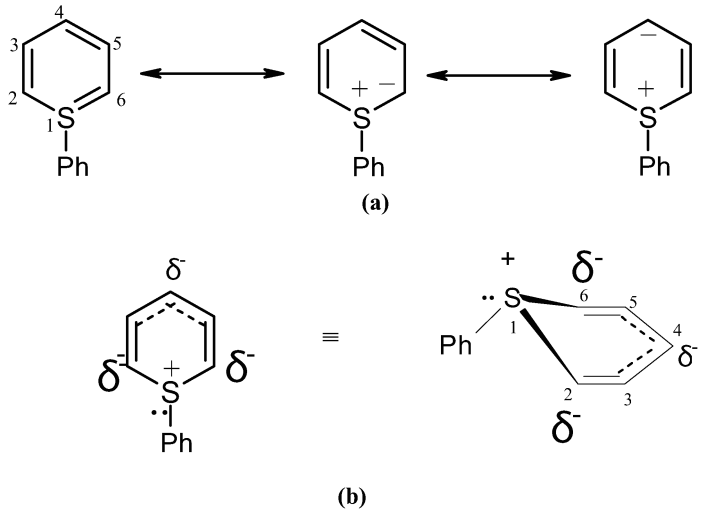
The calculations show that compounds **1–4** adopt boat conformation (Figure 1).

The electronic thermal energies (E), thermal enthalpies (H), and thermal free energies (G) are calculated for **1–4** at HF/6–311+G* and B3LYP/6–311+G* levels of theory (Table I). It was previously reported that 1-thianaphthalene is more stable than 2-thianaphthalene (3.1 kcal/mol).[14] Similarly, compound **2** is more stable than its isomer **3** (2.6 kcal/mol calculated by DFT, Table I). This may be due to the higher importance of resonance in the ring of **2** with respect to **3**.

The charges at the atoms in **1–4** are presented in Table II. The positive charge at the sulfur atom increases in the series **1** < **2** < **4** (Table II). This changes of the positive charge at the sulfur atom are consistent with those of the parent H-substituted compounds in this order: thiabenzene < 1-thianaphthalene < 9-thiaanthracene).[14] The positive charge at the sulfur atom is highest in the phenyl substituted derivatives **1–4** as compared to the corresponding H-substituted compounds. Furthermore, the positive charge at the sulfur atom is highest in **1** as compared to *S*-methylthiabenzene and thiabenzene.[14, 15] The different charge distribution at the atoms in **3** with respect to that in **1**, **2**, and

TABLE II Charge Distribution and Dipole Moment of Compounds 1–4 Calculated Using B3LYP Method

	Charge						Total dipole moment (D)
	S_1	C_2	C_3	C_4	C_5	C_6	
1	0.486046	–0.24897	0.089944	–0.08427	0.086015	–0.26619	1.3943
2	0.490355	–0.37759	0.215332	0.069308	0.058393	–0.21598	1.8545
3	0.484775	–0.29427	0.074016	–0.14372	0.218759	–0.20753	2.3946
4	0.492575	–0.2457	0.233028	–0.24686	0.23304	–0.24577	2.8212



SCHEME 2 (a) Resonance structures showing the negative charge at C_2 and C_4 in *S*-phenyl-thiabenzene. (b) The bond order with delocalization of the negative charge at C_2, C_6 and C_4 for *S*-phenyl-thiabenzene.

4 is related to the different position of the sulfur atom in the ring. A positive charge at the sulfur atom introduces ylide character. Compound **4** has a greater ylide character than the other compounds **1–3**. The dipole moment of **4** confirms the larger ylide character (Table II). Hortmann et al. proposed the perfect resonance of negative charge at C_2 and C_4 (Scheme 2a).[20] Nevertheless, the charge distribution at C_2 and C_4 shows partial electron delocalization in the thiabenzene ring (Scheme 2b, Table II).

The bond lengths and bond angles of **1** are more or less similar to those of **4** (Tables III and IV). The similarity between structures **1** and **4** may be the reason for the similar bond lengths and torsion angles in the two compounds. The bond angle $\angle C_2S_1C_6$ in the phenyl substituted compounds **1–4** is smaller than in the corresponding H-substituted derivatives.[14] The dihedral angles indicate a boat conformation for **1–4** (Table V). The dihedral angle $\angle C_2S_1C_6C_5$ in the phenyl substituted compounds **1–4** is smaller than in the corresponding H-substituted derivatives. Also, the dihedral angle $\angle C_2S_1C_6C_5$ is smaller in **1** as compared to *S*-methylthiabenzene and thiabenzene.[14,15] Non-planarity of **1–4** may be explained by orbital non-hybridization.[21] Kutzelnigg gives for the orbital non-hybridization for higher row elements the following reasons:

TABLE III Bond Lengths in Benzene and in Compounds 1–4 Calculated Using HF and B3LYP Methods

	R(1,2)	R(1,6)	R(1,7)	R(2,3)	R(6,5)	R(3,4)	R(4,5)
Benzene	1.3862[a]	1.3862	1.0756	1.3862	1.3862	1.3862	1.3862
	1.3966[b]	1.3966	1.0870	1.3966	1.3966	1.3966	1.3966
1	1.7296	1.7372	1.8152	1.3714	1.3632	1.3927	1.4008
	1.7399	1.7442	1.8706	1.3840	1.3792	1.4018	1.4054
2	1.7023	1.7677	1.8205	1.3968	1.4032	1.3667	1.4360
	1.7147	1.7781	1.8732	1.4014	1.4226	1.3835	1.4304
3	1.6898	1.7621	1.8201	1.4156	1.3346	1.4165	1.4431
	1.7048	1.7711	1.8757	1.4161	1.3555	1.4375	1.4347
4	1.7427	1.7428	1.8201	1.4141	1.4141	1.4047	1.4048
	1.7546	1.7546	1.8654	1.4320	1.4320	1.4099	1.4099

[a]Calculated via HF.
[b]Calculated via B3LYP.

The 3s-AOs are much less diffuse than the 3p-AOs. Consequently, the Pauli repulsions between the XH bond and also between the HX bond and the lone pair in second row elements are necessarily weaker than in first row elements. Finally, because of the different $\langle r \rangle_s$ and $\langle r \rangle_p$ values, the hybridization is also less effective in strengthening the bond.[21]

($\langle r \rangle$ is the distance of the valence electrons from the nucleus.)
The energies of compounds **1–4** as a function of the torsion angle C_2-S_1-C_7-C_8 in the range from 50° to 250° are shown in Figure 2. These scans could give the energy for the rotation barrier of the phenyl ring for **1–4**.

TABLE IV Bond Angles in Benzene and in Compounds 1–4 Calculated Using HF and B3LYP Methods

	A(1,6,5)	A(2,1,7)	A(2,1,6)	A(3,2,1)	A(4,3,2)	A(3,4,5)	A(4,5,6)
Benzene	120.000[a]	120.002	120.000	120.000	120.000	120.000	120.000
	120.002[b]	119.999	120.002	119.997	120.002	120.002	119.997
1	119.624	107.344	102.079	119.572	125.925	119.218	125.676
	119.421	105.675	101.969	119.341	125.201	120.046	125.017
2	118.505	108.794	103.062	118.511	126.070	121.204	122.672
	118.469	107.499	102.737	118.940	125.494	121.806	122.516
3	120.253	111.393	102.354	121.907	122.423	119.720	126.293
	120.535	110.141	101.562	122.530	122.164	119.760	126.167
4	117.600	104.949	103.021	117.599	123.359	122.199	123.358
	118.050	104.103	103.020	118.050	123.046	123.128	123.046

[a]Calculated via HF.
[b]Calculated via B3LYP.

TABLE V Dihedral Angles in Benzene and in Compounds 1–4 Calculated Using HF and B3LYP Methods

	D(2,1,6,5)	D(3,2,1,7)	D(3,2,1,6)	D(4,3,2,1)	D(3,4,5,6)	D(5,4,3,2)	D(7,1,6,5)
benzene	0[a]	180	0	0	0	0	180
	0[b]	180	0	0	0	0	180
1	−27.171	−85.0972	26.1061	−8.8834	12.2233	−13.4632	85.0608
	−29.0879	−81.5146	28.4417	−10.6912	12.4591	−13.1811	81.083
2	−29.9024	−77.6829	30.6696	−12.5945	13.9664	−13.5219	83.0861
	−30.2705	−75.8916	31.0944	−13.3603	13.0613	−12.6614	80.9803
3	16.6859	154.5198	−28.4507	23.3963	−11.5464	−6.234	−166.516
	16.4523	154.8394	−28.7472	24.4995	−10.744	−7.8572	−167.419
4	−33.9399	5.3891	33.9469	−12.3777	16.7921	−16.7849	75.6828
	−32.8683	5.2774	32.8691	−12.9027	14.6122	−14.6113	75.5496

[a]Calculated via HF.
[b]Calculated via B3LYP.

Compounds **1** and **4** behave similarly and show two minimum energies at 123° and 145° as well as at 160° and 179°, respectively (Figure 2). In contrast, compounds **2** and **3** have a minimum energy at 117° and 118°, respectively. These changes may be related to steric interaction of the phenyl group with the adjacent hydrogen atoms. The energy change

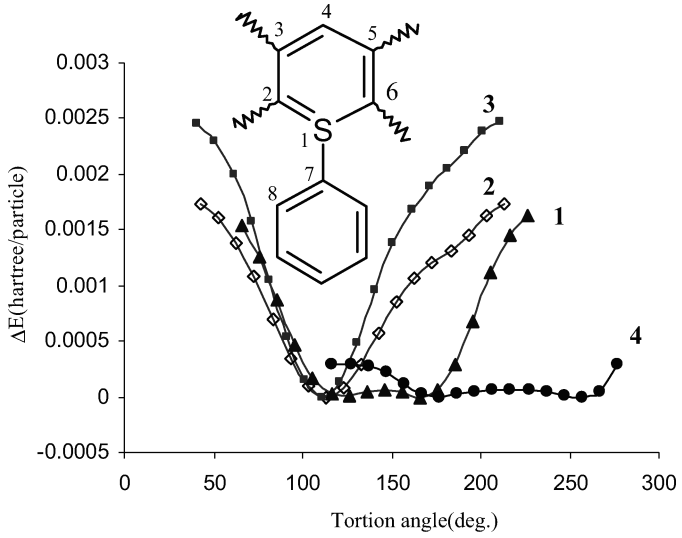


FIGURE 2 Changes of energy (Hartree) as function of the torsion angle C_2-S_1-C_7-C_8 for compounds **1–4**.

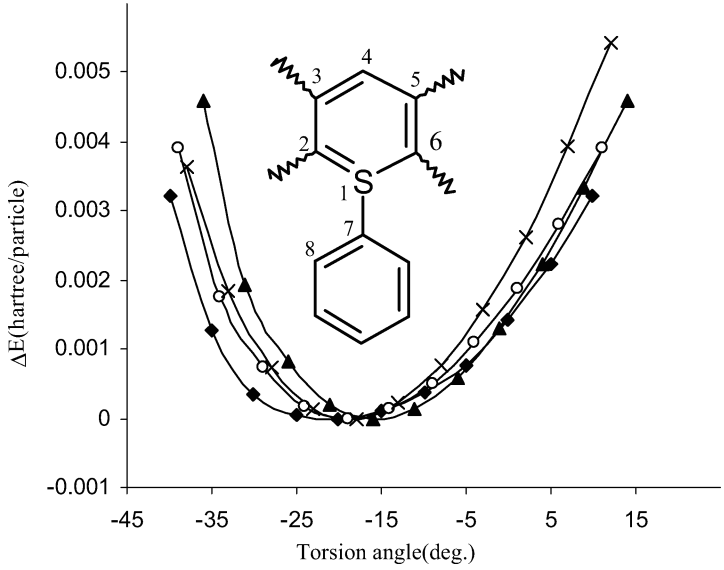


FIGURE 3 Changes of energy (Hartree) as function of the torsion angle S_1-C_2-C_3-C_4 for compounds **1–4.**

in the case of **4** on variation of the dihedral angle is lower than for the other compounds. Molecules **1–4** show a flat energy profile when changing the torsion angle C_2-S_1-C_5-C_6 from –40° to 10°. Their curves are symmetrical (Figure 3).

Thiabenzenes could exist in either planar (Figure 4a) or boat conformations (Figure 4b). The boat conformers of **1–4** are more stable due to the presence 6π electrons in the thiabenzene ring. During the inversion process, the *p* orbital at the sulfur atom containing the unshared

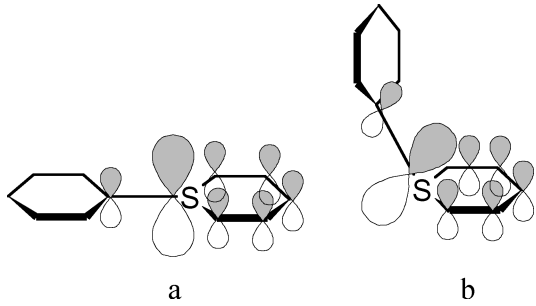


FIGURE 4 (a) Planar conformer and (b) boat conformer of *S*-phenylthiabenzene **1**.

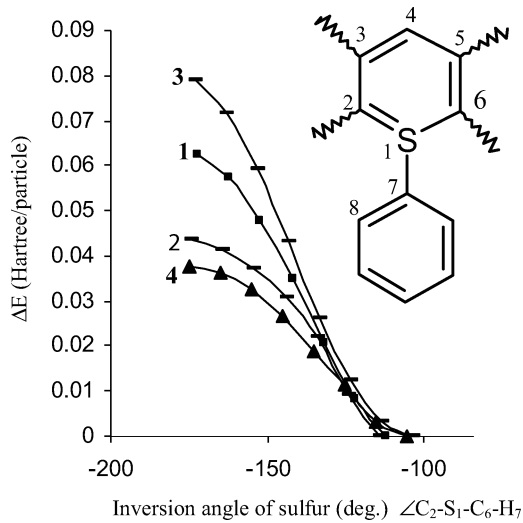


FIGURE 5 Changes of inversion barrier energy (Hartree) as function of $\angle C_2$-S_1-C_6-H_7 for compounds **1–4**.

electrons becomes parallel to the adjacent *p* orbitals at the carbon atoms. This leads to a strong repulsive interaction and thus to instability. In the planar conformer the unshared electrons at the sulfur atom take part in a cyclic delocalized π-system, which is anti-aromatic and unstable because of the presence of 8π electrons in the thiabenzene ring. A variation of the torsion angle ($\angle C_2$-S_1-C_6-H_7) was carried out in order to study the activation energy for the inversion at sulfur atom in compounds **1–4**, which decreases in the order **3** > **1** > **2** > **4** (Figure 5). The activation energy for the inversion at the sulfur atom in compounds **1–4** is less than in the corresponding H-substituted system. The lowest inversion barrier is found for compound **4** and indicates the importance of the aromatic character in constructing the planarity of the conformer. On the other hand, the highest inversion barrier resulting for compound **3** is due to its lower aromatic character and the higher steric repulsion as compared to compound **2**.

CONCLUSIONS

We have provided reasonable evidence for a bonding model for *S*-phenyl-thiabenzene **1**, *S*-phenyl-1-thianaphthalene **2**, *S*-phenyl-2-thianaphthalene **3**, and *S*-phenyl-9-thiaanthracene **4**, which is consistent with experimental observations. The boat conformers of compounds **1–4** are homo-aromatic and more stable due to the 6π electrons

in their thiabenzene ring. The positive charge at the sulfur atom increases in the series **1** < **2** < **4**. The activation energy for the inversion at the sulfur atom in compounds **1–4** decreases in the order of **3** > **1** > **2** > **4**.

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