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Theoretical Studies on Thiabenzene and Its Fused Derivatives: DFT and Ab Initio Computations

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ABSTRACT: *The molecular structures of thiabenzene (**1**), 1-thianaphthalene (**2**), 2-thianaphthalene (**3**), and 9-thiaanthracene (**4**) are studied using HF and DFT methods with 6-31+G* basis set. The nonplanar boat conformers of **1–4**, with 6π-electrons in their heterocyclic ring, appear more stable than the corresponding planar conformers with 8π-electrons in the ring. This study focuses on the stability, the ylide character, the inversion barrier energy of sulfur atoms, and the conformational flexibility of the ring in **1–4**.* © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:376–381, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20214

INTRODUCTION

Thiabenzenes were first reported by Price in 1961 [1]. 1,2,4,6-Tetraphenylthiabenzene was prepared through the reaction between 2,4,6-triphenylthiopyrylium perchlorate and phenyllithium. Thiabenzenes are of interest to chemists because of their in situ generation and Stevens rearrangement to thiopyrans [2–11]. Thiabenzenes are thermodynamically unstable. Treating them with oxygen and hydrogen chloride yields oxypyrylium zwitterions. Thiabenzene system has many unusual properties. It shows aromatic character. Its dipole moment (1.88 D) is lower than the open chain ylides [2]. It is soluble in nonpolar solvents and appears with an intense purple color [2].

1- and 2-thianaphthalenes and 9-thiaanthracene show properties similar to thiabenzenes. They are, however, more stable and do not react with oxygen and hydrogen chloride gas [2]. The derivatives of thiabenzenes are also synthesized and the effects of electron donating and withdrawing groups on them are studied [4–8]. Here, we are interested in the intramolecular conversion of thiabenzenes to 4H- and 2H-thiopyrans [12–15]. Therefore, following-up our previous work [16], we report the ab initio and DFT calculation on thiabenzene and its fused analogues.

METHOD OF CALCULATIONS

The molecular structures of **1–4** are scrutinized (Scheme 1). Geometrical optimizations are carried out using HF and DFT methods with 6-31G* and 6-31+G* basis sets [17–19]. All calculations are performed using Gaussian 98 program on a Pentium-4 computer [20].

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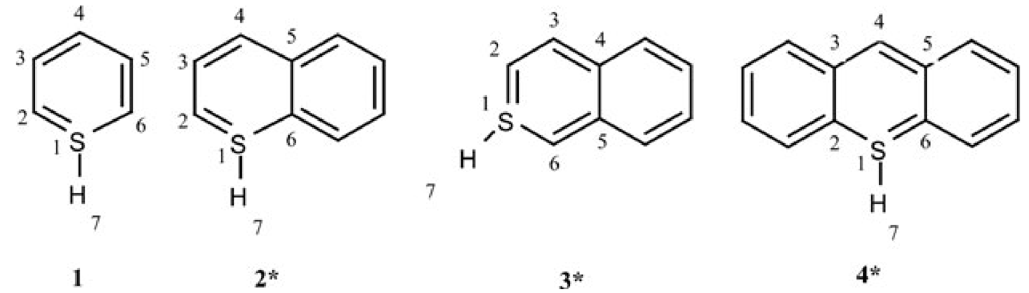


SCHEME 1 Thiabenzene (**1**), 1-thianaphthalene (**2**), 2-thianaphthalene (**3**), and 9-thiaanthracene (**4**). *In order to simplify the comparison, the same numbering used for **1** are employed in **2, 3**, and **4**.

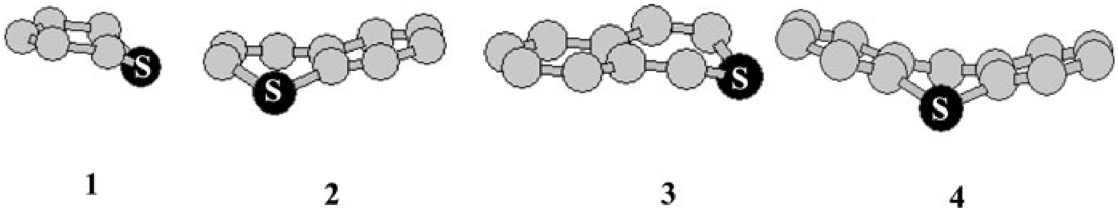


FIGURE 1 Optimized conformations of **1–4** using B3LYP/6-31+G* level. Black balls are sulfur atom, and gray balls are carbons. The hydrogen atoms are not shown.

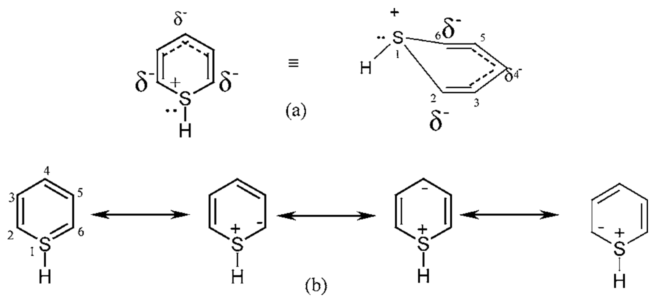
TABLE 1 HF and B3LYP Data (kcal/mol) Consisting of the Thermal Energies (*E*), Thermal Enthalpies (*H*), Thermal-Free Energies (*G*) for Optimized Conformations of Thiabenzene (**1**), 1-Thianaphthalene (**2**), 2-Thianaphthalene (**3**), and 9-Thiaanthracene (**4**) using 6-31+G* Basis Set

	HF			*B3LYP*		
Comp.	*E*	*H*	*G*	*E*	*H*	*G*
1	−370236.30	−370235.18	−370276.23	−371502.66	−371501.54	−371543.45
2	−465966.15	−465965.03	−466012.98	−467858.67	−467857.55	−467906.74
3	−465962.83	−465961.72	−466009.79	−467855.58	−467854.46	−467903.63
4	−561691.36	−561690.24	−561744.92	−564297.87	−564296.75	−564353.42

RESULTS AND DISCUSSION

Thiabenzene (**1**), 1-thianaphthalene (**2**), 2-thianaphthalene (**3**), and 9-thiaanthracene (**4**) have 6π-electrons with ylide character in the S-ring (Scheme 1). These compounds seem to prefer a boat conformational structure (Fig. 1). The electronic thermal energies (*E*), thermal enthalpies (*H*), and thermal free energies (*G*) are calculated for **1–4** at HF/6-31+G* and B3LYP/6-31+G* levels of theory (Table 1). Compounds **2** and **3** have identical molecular formula, but the stability of **2** is more than **3** ($\Delta G = 3.11$ kcal/mol, calculated using the DFT method, Table 1). This may be due to the higher importance of resonance in S-ring of **2**.

It is previously reported that two main canonical forms can be considered for sulfur as well as phosphorous ylides, because of d_π-p_π bonding (Scheme 2) [3]. However, we did not observed any d_π-p_π or p_π-p_π bonding between sulfur and adjacent carbon atoms using NBO and bond order calculations on **1** at B3LYP/6-31+G* level of theory. The bond orders of thiabenzene are C_2—S_1 (0.728), C_2=C_3 (1.164), C_3—C_4 (1.073) (Scheme 2a). The double bond is formed



SCHEME 2 (a) The bond order with partial resonance of negative charge on C_2, C_6, and C_4 for thiabenzene. (b) The complete resonance of negative charge on C_2 and C_4 for thiabenzene.

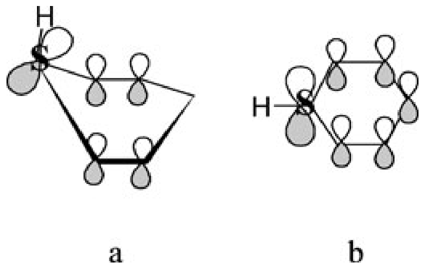


FIGURE 2 (a) Boat conformer of thiabenzene, **1**; (b) planar conformer of thiabenzene, **1**.

between C_2 and C_3 as well as C_5 and C_6. Quasi-double bond is formed between C_3 and C_4 as well as C_4 and C_5. The p_π-p_π bond is formed between C_2 and C_3. The bond–bond hybridizations for **1** are S_1—C_2 ($sp^{3.53}$—$sp^{3.07}$), C_2=C_3 ($sp^{1.42}$—$sp^{1.76}$, p_π-p_π), and C_3—C_4 ($sp^{1.74}$—$sp^{1.82}$). Also, these bond–bond hybridizations confirm the formation of p_π-p_π bonding between the C_2 and C_3.

Thiabenzenes could exist in either boat (Fig. 2a) or planar conformations (Fig. 2b). The boat conformers of **1–4** are homoaromatic and relatively more stable for having 6π-electrons in their S-ring. In the inversion process, *p* orbital on sulfur atom containing unshared electrons becomes parallel with the adjacent *p* orbitals on the carbons. This leads to a strong repulsive interaction and instability. In the planar conformer (Fig. 2b), the unshared electrons on the sulfur atom take part in a continuous cyclic delocalized system which is antiaromatic and unstable for having 8π-electrons in the S-ring. Scanning the torsion angle ($\angle C_2$–S_1–C_6–H_7) is carried out in order to study the inversion barrier energy of sulfur atom in **1–4** which shows an inversion barrier energy trend of **3** > **1** > **2** > **4** (Fig. 3). The lowest inversion barrier energy for **4** indicates the importance of aromatic character in constructing the planarity of the conformer. On the other hand, the highest inversion barrier energy for **3** is due to its lower aromatic character and higher steric repelling than **2**. The order of inversion energy barrier (**3** > **1** > **2** > **4**) is further confirmed through the calculations of the differences between the optimized planar structures (transition states) and their corresponding boat minima (Table 2).

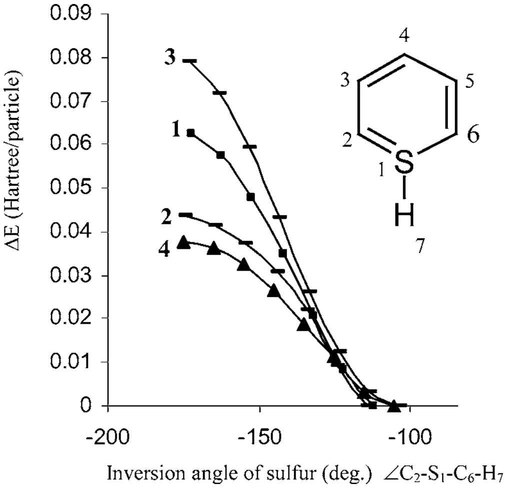


FIGURE 3 Changes of inversion barrier energy (Hartree) vs. the $\angle C_2$—S_1—C_6—H_7 angle for **1–4**.

A homodesmic reaction is applied to quantification of stability and extends of homoaromaticity character [21]. The heat of isodesmic and/or homodesmic (formal) reaction is systematically used as a measure of aromaticity and to quantification of structure–stability relationships [22]. Subtracting the energies of starting materials (**1–4** and C_4H_6) from the corresponding homodesmic products (**1′–4′**) are related to the relative stabilities and homoaromaticity character for **1–4** (Scheme 3 and Table 3). The relative stability, ΔE_T, for each species (using B3LYP/6-31+G* level) is **4** (−46.392 kcal/mol) > **2** (−14.622 kcal/mol) > **3** (−12.637 kcal/mol) > **1** (−9.548 kcal/mol). These results are consistent with those of Price and coworkers experimental data about the stabilities of **4** and **2** with respect to **1**. Molecules **1**, **2**, and **4** are found to have a flat minimum energy at −20° when scanning torsional angle $\angle C_2$—S_1—C_6—C_5 is from −40° to 10° (Fig. 4). Their curves are symmetrical.

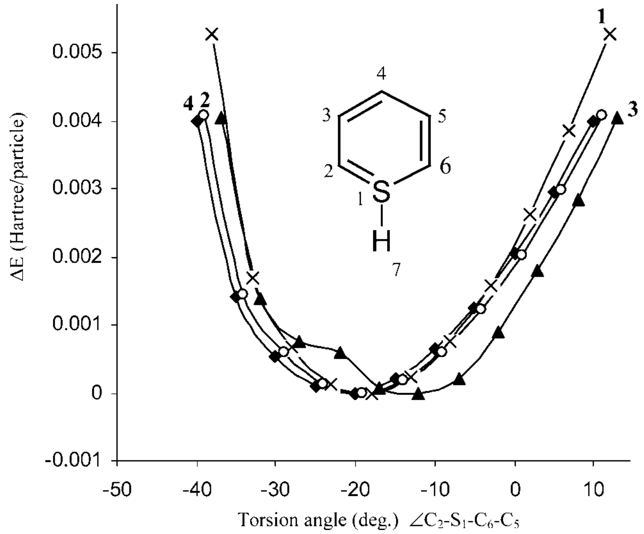
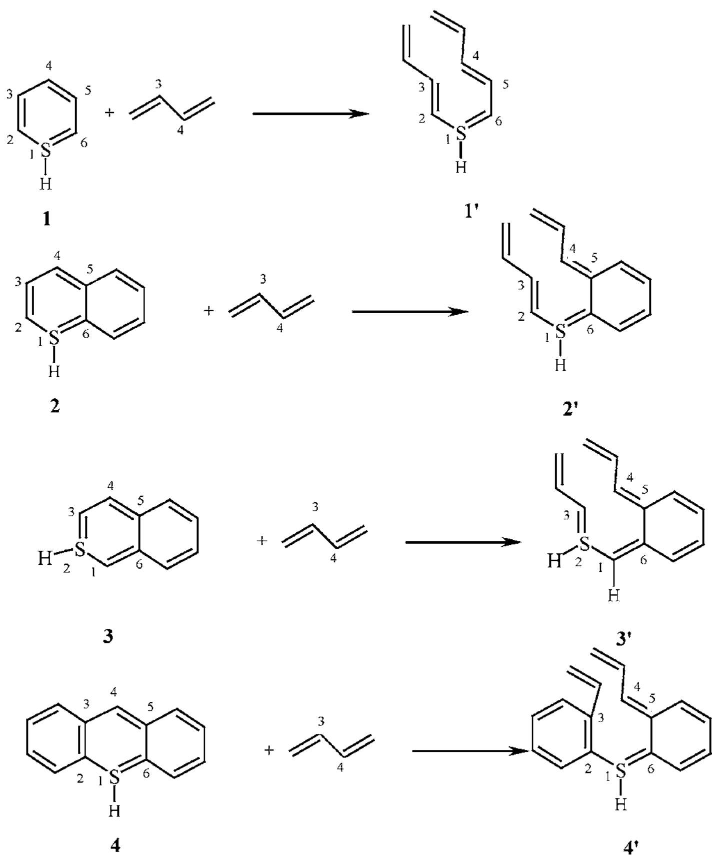


FIGURE 4 Changes of energy (Hartree) vs. the torsion angle $\angle C_2$—S_1—C_6—C_5 for **1–4**.



SCHEME 3 Homo-desmic reaction between starting materials (**1**–**4** and C_4H_6) and its corresponding product **1**′–**4**′.

TABLE 2 The Single Point and Total Optimization Energies and Differences of Single Point and Total Optimization Energies for Thiabenzene (**1**), 1-Thianaphthalene (**2**), 2-Thianaphthalene (**3**), and 9-Thiaanthracene (**4**) at B3LYP/ 6-31+G* Level of Theory

Compound	*Energy of the Nonplanar Minima (E_1) (kcal/mol)*	*Energy of the Planar Transition States (E_2) (kcal/mol)*	$\Delta E_{(E2-E1)}$ *(kcal/mol)*
1	−371625.638	−371555.683	69.955
2	−468043.303	−467974.366	68.937
3	−468039.283	−467968.845	70.438
4	−564457.119	−564390.037	67.082

TABLE 3 Total Energies (E_T, kcal/mol) for **1**–**4** and **1**′–**4**′ along with ΔE_T (kcal/mol) between Starting Materials (**1**–**4** and C_4H_6) and Product (**1**′–**4**′) Using Homodesmic Reaction Shown in Scheme 3 with 6-31+G* Basis Set

	E_T			E_T		ΔE_T	
Reactants	*HF*	*B3LYP*	*Products*	*HF*	*B3LYP*	*HF*	*B3LYP*
1	−371568.986	−370310.889	**1**′	−469397.168	−467462.076	−14.028	−9.548
2	−467957.354	−466077.397	**2**′	−565780.463	−563225.328	−17.284	−14.622
3	−467953.519	−466073.511	**3**′	−565778.613	−563224.217	−14.509	−12.637
4	−564341.991	−561839.196	**4**′	−662133.330	−658976.480	−27.930	−46.392
			C_4H_6	−97165.215	−97837.731	—	—

TABLE 4 Mulliken Charge Distribution and Dipole Moment for **1–4** Calculated at B3LYP/ 6-31+G* Level of Theory

	Charge						
Compounds	*S_1*	*C_2*	*C_3*	*C_4*	*C_5*	*C_6*	*Total Dipole Moment*
1	0.393	−0.242	0.097	−0.103	0.097	−0.242	0.824
2	0.385	−0.348	0.218	0.057	0.072	−0.217	1.198
3	0.392	−0.261	0.083	−0.157	0.224	−0.213	1.658
4	0.420	−0.232	0.237	−0.264	0.237	−0.232	1.848

TABLE 5 Bond Lengths (*R*)/Angstrom for **1–4** Calculated at HF/6-31+G* (the first line) and at B3LYP/6-31+G* (the second line)

Compounds	*R(1,2)*	*R(1,6)*	*R(1,7)*	*R(2,3)*	*R(6,5)*	*R(3,4)*	*R(4,5)*
1	1.733	1.733	1.349	1.365	1.365	1.401	1.401
	1.743	1.743	1.401	1.378	1.378	1.408	1.408
2	1.700	1.765	1.351	1.394	1.402	1.371	1.440
	1.712	1.781	1.404	1.398	1.420	1.387	1.436
3	1.685	1.762	1.357	1.416	1.334	1.418	1.447
	1.699	1.774	1.418	1.416	1.353	1.439	1.440
4	1.743	1.743	1.346	1.411	1.411	1.409	1.409
	1.756	1.756	1.395	1.428	1.428	1.416	1.416

TABLE 6 Bond Angles (A)/degree for **1–4** Calculated at HF/6-31+G* (the First Line) and at B3LYP/ 6-31+G* (the Second Line)

Compounds	*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)*
1	116.728	101.575	103.541	116.728	125.380	119.568	125.380
	117.098	101.185	103.034	117.098	124.908	120.099	124.908
2	116.552	104.938	104.035	116.472	125.523	121.432	122.491
	116.558	104.678	103.346	117.129	125.018	121.867	122.400
3	118.150	108.857	103.137	119.567	121.899	119.992	126.109
	118.702	109.330	102.066	120.560	121.621	119.913	126.088
4	116.065	99.840	104.010	116.065	123.106	122.250	123.106
	115.933	98.202	103.761	115.933	122.670	122.932	122.670

TABLE 7 Dihedral Angles (*D*)/degree for **1–4** Calculated at HF/6-31+G* (the First Line) and at B3LYP/6-31+G* (the Second Line)

Compounds	*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)*
1	−33.073	−71.997	33.073	−10.913	17.890	−17.891	71.996
	−33.633	−70.769	33.633	−11.751	17.178	−17.178	70.769
2	−33.531	−65.635	36.006	−15.182	18.076	−15.680	73.913
	−34.193	−63.688	36.407	−15.672	17.071	−15.203	72.504
3	−20.787	−152.089	35.678	−28.534	15.671	6.039	167.650
	−21.107	−153.845	35.668	−28.773	14.573	7.107	169.256
4	36.400	−4.084	−36.400	11.858	−20.270	20.2702	−66.429
	37.511	−4.156	−37.511	12.752	−19.974	19.974	−63.074

Compounds **1–4** are of a particular interest because they could have different substituents on the S-ring. The positive charge on the sulfur atom, in contrast to the negative charge on the adjacent carbons, increases from **1** to **4** (Table 4). Positive charge on sulfur atom introduces the ylide character. The compound **4** has a greater ylide character than **1**. The dipole moment of these compounds confirm extent of ylide character (Table 4). Hortmann and coworkers proposed the perfect resonance of negative charge on C_2, $C_{6,}$ and C_4 (Scheme 2) [23]. Nevertheless, the charge distribution on C_2 and C_4 shows partial electron delocalization in the S-ring (Table 4). The bond lengths and bond angles of **1** are more or less similar to **4** (Tables 5 and 6). Similarity between structures **1** and **4**, it may be the reason for their similarity of the bond lengths and torsional angles. The dihedral angles indicate a boat conformational structure for **1–4** (Table 7). Unshared electrons on sulfur and the ylide character as well as the low overlap between sulfur and carbon orbitals may be the reasons for boat structures in **1–4**.

CONCLUSION

Reasonable evidence for bonding models of thiabenzenes **1–4** is provided which are consistent with experimental observations. These molecules are more stable in nonplanar boat conformation compared to the planar. The lowest inversion barrier energy is found for **4** than others among **1–4**. The relative stability of thiabenzenes **1–4** show that thiaanthracene is more stable than others through homodesmic reaction. The stability order at B3LYP/6-31+G* levels of theory is **4** (−46.392 kcal/mol) > **2** (−14.622 kcal/mol) > **3** (−12.637 kcal/mol) > **1** (−9.548 kcal/mol).

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