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Theoretical Study on S-Methyl-thiabenzene and Their Analogue *via* DFT Method

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Molecular structures of S-methyl-thiabenzene and their analogue, $1_{Me(H)}$–$3_{Me(H)}$ are studied using *ab initio* calculations with DFT method and 6–311++G** basis set. These compounds have 6π-electrons with homoaromatic and ylide character. In contrast to planar conformer, the pyramidal conformer of $1_{Me(H)}$–$4_{Me(H)}$ is stable. The nature of structural bonds is investigated.

Key Words: ***ab initio*, Ylide character, S-methyl-thiabenzene, Homoaromatic character, DFT.**

INTRODUCTION

Ylides are defined as compounds in which a positively charged atom from group V or VI is connected to carbon atom carrying an unshared pair electron. Some ylides are phosphorus[1], nitrogen[2], sulfur[3], arsenic[4] and selenium[5]. Because of pπ-dπ bonding, two canonical forms can be written for phosphorus and sulfur ylides, but there is only one form for nitrogen ylides. Although the use of phosphorus ylides is the most widespread, interest in the applications of sulfur ylides to synthetic problems has been stimulated by the work of Corey[6]. Recently, Lloyd and coworkers[5, 7, 8] have prepared a series of heteronium ylides of groups V and VI including selenium and tellurium. Mono-ylides of arsenic[9–12] found thermally quite unstable materials. In follow-up on our work[13, 14], we comparatively studied some properties (ylidic character and nature of bonds) of $1_{Me(H)}$–$3_{Me(H)}$.

EXPERIMENTAL

Method of calculation

The molecular structures of $1_{Me(H)}$–$3_{Me(H)}$, shown in **Scheme-1**, are studied using *ab initio* methods. Geometry optimizations are performed by B3LYP[15, 16] methods using 6–311++G** basis set of the *Gaussian* 98 system of programs[17]. The geometry will be adjusted until a stationary point on the potential surface is found. Here, the Berny algorithm is employed for all minimizations, using redundant internal coordinates[18].

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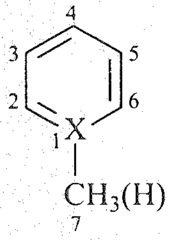
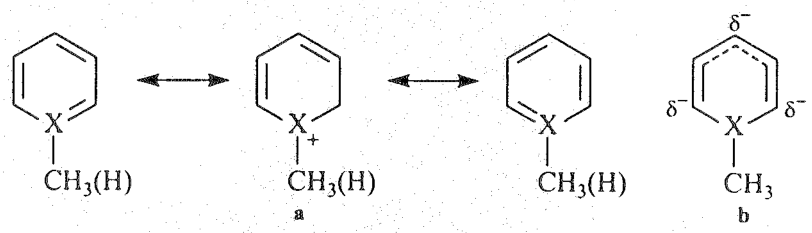


X = O, $1_{Me(H)}$; S, $2_{Me(H)}$; Se, $3_{Me(H)}$

Scheme-1. Derivatives of S-methyl-thiabenzene and their analogue $1_{Me(H)}$–$3_{Me(H)}$

RESULTS AND DISCUSSION

S-methyl-thiabenzene and their analogue, $1_{Me(H)}$–$3_{Me(H)}$, have 6π-electrons with homo-aromatic and ylide character. The results are consistent with experiments about stability of some ylides[19]. It was reported that two canonical forms (**Scheme-2,** ylide and ylene forms) can be suggested for phosphorus and sulfur because of pπ-dπ bonding, but there is only one form for nitrogen and oxygen. This leads to instability of nitrogen and oxygen ylides. However, the bond orders show a single bond for X_1—C_2, double bond for C_2—C_3 and quasi double bond for C_3—C_4 (**Scheme-2b,** Table-1). Also NBO analysis does not show any d orbital on X_1.



X = 0.1 Me(H), 5.2 Me(H), So 3 Me(H)

Scheme-2. Ylide and aromatic character of thiabenzene derivatives: (a) the perfect resonance of negative charge on C_2 and C_4; (b) the partial resonance of negative charge on C_2 and C_4

TABLE-1
B3LYP/6-311++G** CALCULATED BOND ORDERS FOR $1_{Me(H)}$–$3_{Me(H)}$

Compd.	X—C_7	C_1—X_2	C_2=C_3	C_3—C_4
1_{Me}	0.598	0.567	1.204	1.040
1_H	0.553	0.556	1.208	1.035
2_{Me}	0.610	0.749	1.168	1.051
2_H	0.565	0.742	1.174	1.046
3_{Me}	0.590	0.762	1.169	1.051
3_H	0.568	0.751	1.174	1.047

Therefore, pπ-dπ bond is not formed between X_1 and C_2 as well as between X_1 and C_6.

Compounds $1_{Me(H)}$–$3_{Me(H)}$ could be in two pyramidal and planar conformers (Fig. 1). The pyramidal form is more stable than planar form. In inversion process between pyramidal forms (Fig. 1a) and planar form (Fig. 1b), *p*-orbital on sulfur atom containing unshared electrons becomes parallel to adjacent *p*-orbitals on the two carbons. This leads to strong repulse interaction and diminishes the conjugation of *p*-electrons. Conjugation of 8π-system in the ring tends to planarity but constructs an antiaromaticity system. Therefore, planar conformer has eight-electrons, anti-aromatic and unstable.

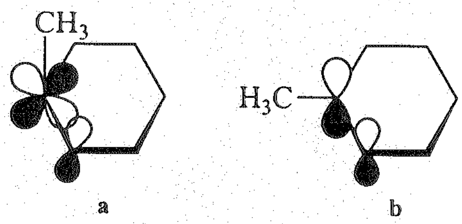


Fig. 1. Two possibilities for construction of 1_{Me}–3_{Me}: (a) pyramidal conformer, (b) planar conformer

The HOMO-LUMO energy separation has been used as a simple indicator of kinetic stability[20] (Table-2). A large HOMO-LUMO gap implies high kinetic stability and low chemical reactivity, because it is energetically favourable to add electrons to a high-lying LUMO and to extract electrons from a low-lying HOMO. A large HOMO-LUMO gap for 1_{Me}–3_{Me} with respect to 1_H–3_H could show the high stability of 1_{Me}–3_{Me} more than 1_H–3_H. It seems that the exchange of hydrogen with methyl group on sulfur atom leads to stability of S-methyl through hyper-conjugation of methyl group with sulfur atom. Also, we could conclude that the $2_{Me(H)}$ is more stable than their corresponding analogues $1_{Me(H)}$ and $3_{Me(H)}$.

TABLE-2
B3LYP/6–311++G** CALCULATED FROM THE HIGHEST OCCUPIED MOLECULAR ORBITAL (HOMO) ENERGIES (eV) AND THE LOWEST UNOCCUPIED MOLECULAR ORBITAL (LUMO) FOR $1_{Me(H)}$–$3_{Me(H)}$

Compd.	B3LYP/6–311++G**		
	HOMO	LUMO	$\Delta_{LUMO\text{-}HOMO}$
1_{Me}	–0.164	–0.012	0.153
1_H	–0.172	–0.026	0.145
2_{Me}	–0.179	–0.025	0.154
2_H	–0.186	–0.035	0.151
3_{Me}	–0.174	–0.026	0.148
3_H	–0.181	–0.037	0.143

Compounds of $1_{Me(H)}$–$3_{Me(H)}$ would have different proton substitution on the ring. The order of NBO charge changes on X_1 (with the B3LYP/6–311++G** level) is: 3_{Me} (0.978) > 2_{Me} (0.807) > 1_{Me} (–0.439) and 3_H (0.812) > 2_H (0.651) > 1_H (–0.521) (Table-3). These orders show that the selenium atom has more charge due to its electropositivity. The positive charge on selenium and negative charge on the adjacent two carbon atoms of $3_{Me(H)}$ explain their high ylide character.

TABLE-3

B3LYP/6–311++G** CALCULATED NBO CHARGES ON ATOMS FOR $1_{Me(H)}$–$3_{Me(H)}$

Compd.	B3LYP/6–311++G**						
	X_1	C_2	C_3	C_4	C_5	C_6	C_7
1_{Me}	–0.439	–0.063	–0.235	–0.418	–0.235	–0.063	–0.184
1_H	–0.521	–0.064	–0.233	–0.426	–0.233	–0.064	0.490
2_{Me}	0.807	–0.540	–0.174	–0.366	–0.174	–0.540	–0.737
2_H	0.651	–0.531	–0.170	–0.364	–0.170	–0.531	0.038
3_{Me}	0.978	–0.582	–0.178	–0.365	–0.178	–0.582	–0.799
3_H	0.812	–0.576	–0.175	–0.361	–0.175	–0.577	–0.019

The geometrical parameters are presented in Table-4. The bond lengths of (H)C_7–X_1 and X_1—C_2 increase from $1_{Me(H)}$ toward $3_{Me(H)}$. This is reasonably due to atomic volume and electropositivity of heteroatom (X_1). The bond angles C_1—C_2—C_3, C_2—C_3—C_4 and C_3—C_4—C_5 in contrast to C_2—X_1—C_6 increase from $1_{Me(H)}$ toward $3_{Me(H)}$. The decreasing of C_2—X_1—C_6 from $1_{Me(H)}$ toward $3_{Me(H)}$ is related to high *p* character sharing of selenium atom with respect to sulfur and oxygen atoms. The dihedral angles of C_3—C_2—X_1—C_6, X_1—C_2—C_3—C_4, C_2—C_3—C_4—C_5 and C_2—X_1—C_6—C_7 decrease from $1_{Me(H)}$ toward $3_{Me(H)}$. These orders show that the C=X—C—C dihedral angle for $1_{Me(H)}$–$3_{Me(H)}$ is out-of-plane. Unshared electrons on sulfur and ylide character may be the reason for the pyramidal structure of $1_{Me(H)}$–$3_{Me(H)}$. The decreasing of dihedral angle C_2—X_1—C_6—C_7 from $1_{Me(H)}$ toward $3_{Me(H)}$ may be related to the increasing *p*-character from oxygen toward selenium.

TABLE-4

B3LYP/6–311++G** CALCULATED GEOMETRICAL PARAMETERS (BOND LENGTHS (R) (Å), BOND ANGLES (A) (°) AND DIHEDRAL ANGLES (D) (°) OF $1_{Me(H)}$–$3_{Me(H)}$

Compd.	B3LYP/6–311++G**											
	$R_{1,7}$	$R_{1,2}$	$R_{2,3}$	$R_{3,4}$	$A_{6,1,2}$	$A_{1,2,3}$	$A_{1,2,3}$	$A_{3,4,5}$	$D_{3,2,1,6}$	$A_{1,2,3,4}$	$D_{2,3,4,5}$	$D_{2,1,6,7}$
1_{Me}	1.474	1.474	1.362	1.410	110.803	114.981	121.823	115.870	45.456	–15.453	–16.020	–128.385
1_H	0.976	1.485	1.360	1.413	110.291	112.928	121.527	115.931	50.434	–16.217	–18.962	–117.500
2_{Me}	1.862	1.748	1.377	1.404	101.672	119.069	125.156	120.041	30.028	–11.780	–13.510	107.413
2_H	1.401	1.746	1.374	1.408	102.441	116.982	124.777	119.999	35.051	–12.281	–17.959	–102.980
3_{Me}	2.021	1.886	1.375	1.404	98.072	119.785	126.987	121.620	24.056	–9.742	–12.071	103.428
3_H	1.538	1.886	1.372	1.407	98.501	118.040	126.795	121.499	29.207	–10.874	–16.168	–100.355

Conclusions

We have reasonably provided evidence of bonding model for 1-heterocyclic benzenes and their analogue $1_{Me(H)}$–$3_{Me(H)}$ consistent to experimental observation. The molecular structures of S-methyl-thiabenzene and their analogue $1_{Me(H)}$–$3_{Me(H)}$ are studied using *ab initio* calculations with DFT method using 6–311++G* basis set. These compounds have 6π-electrons with homo-aromatic and ylide character. In contrast to planar conformer, the pyramidal conformers of $1_{Me(H)}$–$4_{Me(H)}$ are stable.

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