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# THIACYCLOBUTADIENE AND THIABENZENE

## A COMPARATIVE THEORETICAL ANALYSIS

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**Abstract**—The two title compounds have been investigated theoretically using an *ab initio* SCF-MO treatment at the minimal STO-3G level. It has been found that in the most stable conformation thiacyclobutadiene has all atoms approximately in the same plane except for the H atom bonded to sulphur (i.e. a pyramidal sulphur). On the other hand, in the most stable conformation of thiabenzene, the sulphur atom not only is pyramidal, but also ~10° out of the plane containing the carbon system. The barriers to pyramidal inversion at the sulphur centres are ~48 and ~56 kcal/mol for thiacyclobutadiene and thiabenzene, respectively. The properties of these molecules are rationalized by means of Perturbation Molecular Orbital (PMO) theory.

The study of the chemical and physical properties of thiabenzenes has been the object of several experimental investigations. Recently, evidence has been provided for a similarity between the thiabenzenes and cyclic sulphonium ylides.[1] It has been shown that thiabenzenes are pyramidal at sulphur, with a barrier to pyramidal inversion of at least 23 kcal/mol in the case of a 2-thianaphthalene derivative,[1] and of 19 kcal/mol in the case of a substituted 10-thiaanthracene.[2] However, uncertainties concerning the geometric and electronic structure of thiabenzenes still remain due to the fact that these compounds are inherently unstable, and spectroscopic studies are thus rendered inaccessible. In such cases, theoretical investigations can prove to be extremely useful. Preliminary semiempirical MO (CNDO/2) calculations had indicated a barrier to inversion of *ca.* 43 kcal/mol for S-methyl-thiabenzene[3] and of 36–45 kcal/mol for S-phenylthiabenzene.[4] The present work reports *ab initio* SCF-MO calculations of thiabenzene as well as thiacyclobutadiene, a related sulphur heterocycle whose synthesis (as a trisubstituted derivative) has recently been claimed.[5] On the basis of these computations, an orbital model capable of rationalizing the key electronic features of such molecules has been developed. The results of these studies are presented in detail below.

*Computational method.* In this work, we have employed *ab initio* SCF-MO computations of the restricted Hartree-Fock (RHF) type at a minimal basis set level (STO-3G)[6] for determining the preferred geometry of the sulphur heterocycles thiabenzene and thiacyclobutadiene. In all cases, we have made use of the Gaussian 70 series of programs.[7] In order to test the reliability of the computational method for obtaining accurate molecular geometries in cyclic systems containing a second period heteroatom, we first carried out a preliminary geometry optimization on thiophene, where the computed values can be compared with the experimental ones. In this computation we optimized only the bond lengths and angles of the five ring atoms while we kept fixed at the experimental values the bond lengths and angles involving the H atoms (i.e. $<H_4C_4S$ and $<H_3C_3C_2$). The computed geometric parameters, together with the experimental ones,[8] are listed in Table 1. The overall agreement between experimental and computed values is quite good.

Since the sulphur heterocycles investigated here involve a tricoordinate S atom, it is interesting to recall the STO-3G results for the simplest species of this kind, i.e. $H_3S^+$. This sulphonium ion is found to be pyramidal[9] and the STO-3G inversion barrier (35.35 kcal/mol) agrees well with the corresponding value of 30.0 kcal/mol computed with an extended basis including 3d orbitals.[10] It should also be added that in species containing C–S bonds it seems now well established that 3d orbitals act as polarization functions rather than bonding orbitals.[11] All these findings suggest that the minimal STO-3G basis can provide useful information on the structure of such interesting molecules.

Ab initio *results.* We first computed the optimum geometry of planar thiacyclobutadiene. The optimization was carried out with respect to all geometric parameters except that the C–H bond lengths were kept fixed at the value 1.08 Å. In particular, with reference to Fig. 1, we optimized the following geometric parameters:

$$r(D\text{–}S),\quad r(D\text{–}C_1) = r(D\text{–}C_3),\quad r(C_2\text{–}D),$$

$$<SC_1H_1 = <SC_3H_3 \quad \text{and} \quad r(S\text{–}H).$$

The computed results are listed in the first column in Table 2.

In a second stage, we optimized first the $\alpha$ angle (the complement to 180° of the $DSH_4$ angle), then again the various parameters and, finally, $\alpha$. The corresponding computed results are listed in the second column of

Table 1. Total energy and computed (STO-3G) and experimental geometric parameters[a] of thiophene

| | Computed | Experimental[b] |
|---|---|---|
| $r(C_1-S)$ | 1.7261 | 1.7140 |
| $r(C_1-C_2)$ | 1.3377 | 1.3696 |
| $r(C_2-C_3)$ | 1.4564 | 1.4232 |
| $< C_1SC_4$ | 89.8 | 92.16 |
| $< SC_1C_2$ | 113.6 | 111.47 |
| $< C_1C_2C_3$ | 111.5 | 112.45 |
| Total energy a.u. | -545.09203 | |

a. Bond lengths in Å and bond angles in degrees. $<H_4C_4S$ and $<H_3C_3C_2$ have been fixed at the experimental value.

b. From ref. 8.

Table 2. Computed geometric parameters[a] and energies of various conformations of thiacyclobutadiene

| $\gamma$[b] | 0.0 | 0.0 | -10.0 | -20.0 | +10.0 |
|---|---|---|---|---|---|
| $r(C_1-S)$ | 1.8510 | 1.8487 | 1.8321 | 1.8349 | 1.8325 |
| $r(C_1-C_2)$ | 1.3898 | 1.3818 | 1.3798 | 1.3834 | 1.3789 |
| $r(S-H)$ | 1.3330 | 1.3426 | (1.3426)[d] | (1.3426)[d] | (1.3426)[d] |
| $<C_1SC_3$ | 76.5 | 73.0 | 72.9 | 72.7 | 72.6 |
| $<C_1C_2C_3$ | 111.1 | 105.5 | 104.1 | 103.6 | 103.8 |
| $<SC_1C_2 = <SC_3C_2$ | 86.2 | 90.7 | 91.5 | 91.9 | 91.7 |
| $<SC_1H_1 = <SC_3H_3$ | 128.4 | 126.0 | 125.9 | 125.8 | 125.8 |
| $\alpha$[c] | 0.0 | 77.1 | (77.1)[d] | (77.1)[d] | (77.1)[d] |
| Total Energy (a.u.) | -507.40962 | -507.48520 | -507.48477 | -507.47756 | -507.48127 |
| Relative Energy (kcal/mole) | 47.43 | 0.00 | 0.27 | 4.79 | 2.47 |

a. Bond lengths in Å and bond angles in degrees; the C-H bond lengths have been kept fixed at 1.08 Å.

b. $\gamma$ is the complement to 180° of the $C_2DS$ angle. Positive values correspond to movement on the side containing $H_4$. The optimum value of $\gamma$ is -4.40° with relative energy of -0.31 kcal/mole.

c. $\alpha$ is the complement to 180° of the $DSH_4$ angle.

d. Not reoptimized.

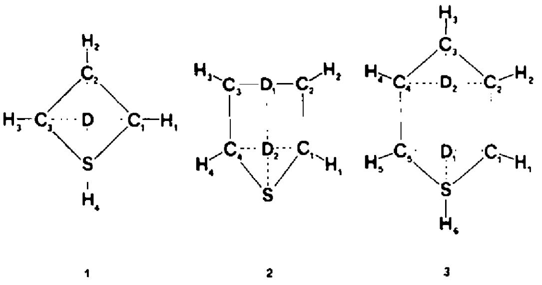

Fig. 1. Numbering convention for the various molecules investigated. The D's denote dummy centers which facilitate the geometry optimization or description.

Table 2. Finally, in a third stage, we reoptimized the various geometric parameters for various values of the angle $\gamma$ (the complement to 180° of the $C_2DS$ angle) around zero. These results are given in the third, fourth and fifth columns of Table 2.

From a comparative analysis of these data, the following observations can be made: (a) The most stable conformation of thiacyclobutadiene corresponds to a structure where all atoms lie approximately in the same plane, except for the H atom bonded to sulphur (pyramidal sulphur) with an out of plane angle $\alpha$ of the order of ~77°. The equilibrium value of $\gamma$ computed by a fit of a cubic curve to $E(\gamma)$ is $-4.4°$ and the energy lowering obtained by moving the S atom out of the plane

Table 3. Computed geometric parameters[a] and energies of various conformations of thiabenzene

| $\gamma^b$ | 0.0 | 0.0 | $-15.0^d$ | $+10.0^d$ | $+15.0^d$ |
|---|---|---|---|---|---|
| $r(C_1-S)$ | 1.7858 | 1.7574 | 1.7876 | 1.7780 | 1.7782 |
| $r(C_1-C_2)$ | 1.3683 | 1.3597 | | | |
| $r(C_2-C_3)$ | 1.3990 | 1.3989 | | | |
| $r(C-H)$ | 1.0830 | 1.0850 | | | |
| $r(S-H)$ | 1.3258 | 1.3671 | | | |
| $<C_1SC_5$ | 105.3 | 103.6 | 101.7 | 101.9 | 101.9 |
| $<C_2C_1S = <C_4C_5S$ | 118.7 | 121.5 | 121.2 | 121.6 | 120.9 |
| $<C_3C_2C_1 = <C_3C_4C_5$ | 128.5 | 126.0 | | | |
| $<C_2C_3C_4$ | 120.4 | 121.6 | | | |
| $<SC_1H_1 = <SC_5H_5$ | 113.7 | 112.6 | | | |
| $<C_1C_2H_2 = <C_5C_4H_4$ | 113.6 | 115.7 | | | |
| $\alpha^c$ | 0.0 | 72.3 | | | |
| Total Energy (a.u.) | -583.41445 | -583.50224 | -583.49780 | -583.50404 | -583.50367 |
| Relative Energy (kcal/mol) | 55.09 | 0.0 | 2.79 | -1.13 | -0.89 |

a. Bond lengths in Å and bond angles in degrees.

b. $\gamma$ is the complement to 180° of the $D_2D_1S$ angle. Positive values correspond to movement on the side containing $H_6$. The optimum value of $\gamma$ is +10.76° with relative energy of -1.14 kcal/mole.

c. $\alpha$ is the complement to 180° of the $D_1SH_6$ angle.

d. Only the $S-D_1$ distance has been optimized, and therefore $r(C_1-S)$, $C_1SC_5$ and $C_2C_1S$ become partially optimized, the remaining parameters kept fixed at the values obtained at $\gamma = 0°$ and $\alpha = 72.3°$.

of the carbon system is 0.31 kcal/mole. (b) The inversion barrier at sulphur is quite high (~48 kcal/mol). (c) The C–S bond lengths are much longer than those in thiophene (Table 1) and this implies that such a bond is more like a single bond (in $CH_3SH$, r(C–S) = 1.804 Å[12]).

Geometry optimization of thiabenzene was carried out by using the same scheme as the one described above. We first optimized the geometric parameters $r(S-C_1) = r(S-C_5)$, $<C_1SC_5$, $r(S-D_2)$, $r(D_2-C_3)$, r(C–H), $r(S-H_6)$, $<SC_1H_1 = <SC_5H_5$, $<C_1C_2H_2 = <C_5C_4H_4$ (Fig. 1) of the planar conformation and the corresponding results are listed in the first column of Table 3.

Subsequently, we optimized $\alpha$ (the complement to 180° of the $D_1SH_6$ angle), again the various parameters and, finally, $\alpha$. The computed values are listed in the second column of Table 3. In a third stage, we computed the energies of conformations at various values of the angle $\gamma$ ($\gamma$ is the complement to 180° of the $D_2D_1S$ angle); therefore in these conformations the S atom is out of the plane containing the carbon system. In this case, we only optimized the $S-D_1$ distance. The results are listed in the other columns of Table 3.

Again, the points of interest are:

(a) The most stable conformation determined by a fit of a cubic curve to $E(\gamma)$, corresponds to a structure with $\gamma = +10.76°$ and therefore, the S atom not only is pyramidal, but is also out of the plane containing the carbon system.

(b) The energy lowering obtained by moving the sulphur atom out of the plane of the carbon system is very small (~1 kcal/mol).

(c) The inversion barrier at sulphur is again quite large (56 kcal/mole). The latter value has been computed assuming the transition state to inversion to be the planar conformation ($\gamma = 0°$). If the transition state to inversion is taken to be the conformation at $\gamma = 10°$, optimizing only the $S-D_1$ distance the inversion barrier becomes 62 kcal/mol.

(d) The C–S bond length decreases in going from the planar to the stable pyramidal conformation and increases again when the sulphur atom is moved out of the plane of the carbon system.

(e) The C–S bond length in the stable conformation is just slightly longer than that in thiophene and, therefore, significantly shorter than that in thiacyclobutadiene. The gross atomic changes of thiacyclobutadiene and of thiabenzene are listed in Table 4.

It is interesting to observe that in the planar conformation both of these molecules display a charge distribution which indicates ylide-like bonding, as represented by a significant positive charge on the sulphur atom and a build-up of a significant negative charge on $C_1$ and $C_3$ in thiacyclobutadiene (Fig. 1), and $C_1$, $C_3$ and $C_5$ in thiabenzene (Fig. 1), in agreement with semiempirical calculations.[4]

*PMO analysis.* In a recent paper,[13] it was suggested that various static and dynamic properties of pentatomic heterocycles can be understood in terms of an orbital model consisting of the $\pi$ orbitals of butadiene interacting with the heteroatom lone pair. This orbital model can be easily applied to thiacyclobutadiene and to thiabenzene. In these cases, the analysis involves the

Table 4. STO-3G gross atomic charges of thiophene, thiacyclobutadiene and thiabenzene in optimized geometry[a]

| Atoms | Thiophene | Thiacyclobutadiene[b] | Thiabenzene[c] |
|---|---|---|---|
| S | +0.258 | +0.344 | +0.457 |
| $C_1$ | -0.179 | -0.260 | -0.251 |
| $C_2$ | -0.084 | -0.015 | -0.015 |
| $C_3$ | -0.084 | --- | -0.194 |
| $H_1$ | +0.070 | +0.054 | +0.049 |
| $H_2$ | +0.064 | +0.063 | +0.070 |
| $H_3$ | +0.064 | +0.054 | +0.027 |
| $H_4$ | +0.070 | +0.020 | +0.049 |
| $H_6$ | --- | --- | +0.034 |

a. For numbering convention, see Figure 1.

b. Values obtained at $\gamma = 0°$.

c. Values obtained at $\gamma = 10°$.

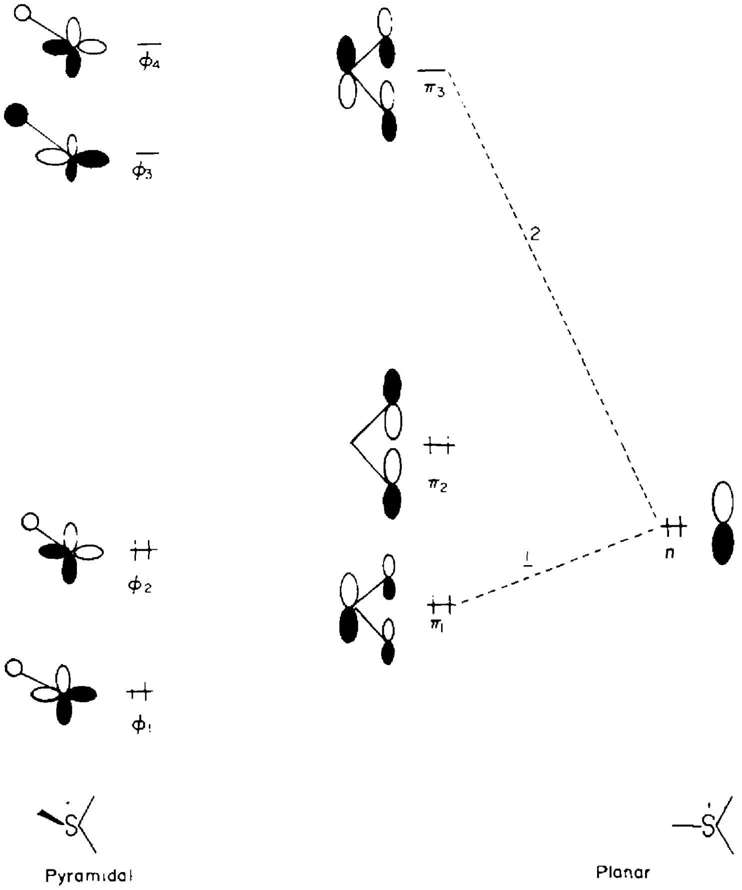

Fig. 2. Interaction diagram between the $\pi$ MO's of the allyl anion and the MO's of the $\rangle S^+$–H fragment.

$\pi$ MO's of the allyl anion and of the pentadienyl anion, respectively, interacting with the $>S^+{-}H$ fragment MO's of suitable symmetry. The key orbital interactions are shown in Figs. 2 and 3. The MO's of the $>S^+{-}H$ fragment have been taken from STO-3G computations of $SH_3^+$.

In the interaction diagrams of Figs. 2 and 3 we distinguish two types of interactions:

(a) Four-electron interactions between occupied MO's. Such interactions lead to net four electron destabilization whose expression† is given below:

$$\Delta E^4_{ij} = \frac{4S^2_{ij}}{1 - S^2_{ij}}(\epsilon - K).$$

In the equation above, $\epsilon$ is the mean of the energies of the two interacting orbitals, $S_{ij}$ is their overlap integral, and K is a constant.

(b) Two-electron interactions between doubly occupied MO's and vacant MO's. Such interactions lead to two-electron stabilization given by the following expression:

$$\Delta E^2_{ij} = \frac{(K - \epsilon_i)^2}{\epsilon_i - \epsilon_j} S^2_{ij}.$$

In the above equation $\epsilon_i$ and $\epsilon_j$ are the energies of the doubly occupied and of the vacant MO's respectively, $S_{ij}$ is their overlap integral, and K is a constant.

We proceed now to the discussion of the orbital diagrams, starting with that concerning thiacyclobutadiene (Fig. 2). In our discussion, it is convenient to examine first the interactions with a planar $>S^+{-}H$ fragment, or, in other words, the $\pi$ interactions occurring in the planar conformation of thiacyclobutadiene. Here, there are two key interactions: a four electron interaction between the sulphur lone pair and the lowest occupied $\pi$ type MO of the allyl anion (interaction 1) and a two-electron interaction between the sulphur lone pair and the LUMO of the allyl anion (interaction 2). Because of the large energy difference between the sulphur lone pair and the LUMO of the allyl anion, the corresponding energy stabilization is small, and slightly less than the energy destabilization arising from interaction 1 as can

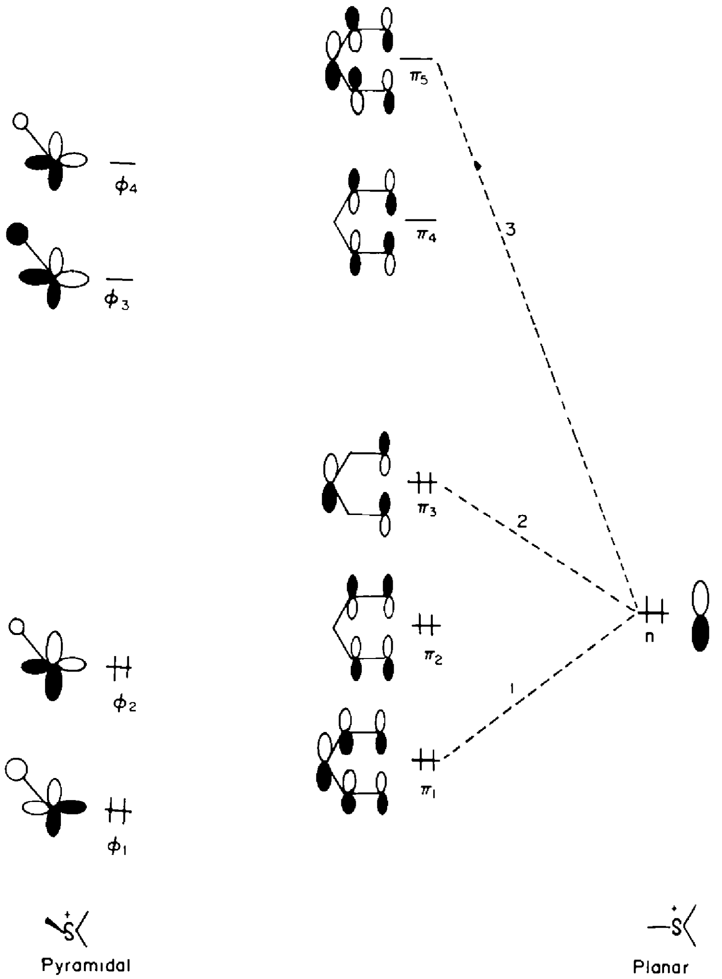

Fig. 3. Interaction diagram between the $\pi$ MO's of the pentadienyl anion and the MO's of the $>S^+{-}H$ fragment.

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†This result is obtained by application of the variational method to the case of two-orbital four-electron interaction and involves no additional assumptions other than the usual approximation of the interaction matrix element as a linear function of the overlap integral.

Table 5. Total and $\pi$-overlap populations for planar and pyramidal thiacyclobutadiene and thiabenzene

| | Planar | | Pyramidal[a] | |
|---|---|---|---|---|
| | Total | $\pi$ | Total | $\pi$ |
| Thiacyclobutadiene | | | | |
| S - $C_1$ | 0.2173 | -0.0004 | 0.2412 | 0.0025 |
| $C_1$ - $C_2$ | 0.5299 | 0.1153 | 0.5194 | 0.1150 |
| Thiabenzene | | | | |
| S - $C_1$ | 0.2549 | -0.0200 | 0.2861 | 0.0101 |
| $C_1$ - $C_2$ | 0.5490 | 0.1389 | 0.5414 | 0.1334 |
| $C_2$ - $C_3$ | 0.4818 | 0.0853 | 0.4890 | 0.0919 |

a. For thiacyclobutadiene, values obtained at $\gamma$ = 0°, for thiabenzene, values obtained at $\gamma$ = 10°.

be inferred from the small negative value of the $\pi$ overlap population of the S–$C_1$ bond (Table 5). Therefore, while this molecule in this conformation should, in principle, be "aromatic" according to Hückel's rule (since it contains 6 $\pi$ electrons), it appears to be "non-aromatic". The following computational results are in agreement with this interpretation: (i) The computed $C_1$–S bond length is appropriate for a single bond. (ii) There is very small electron transfer from suphur to the allyl $\pi$ system, amounting to 0.036 e, while the corresponding value in thiophene, at the same computational level, is 0.23 e.

We now examine the interactions occurring in that conformation of thiacyclobutadiene in which all atoms lie in the same plane, except for the H atom bonded to sulphur. Here, the key orbital interactions are between the $\pi$ MO's of the allyl anion, and the suitable MO's of the pyramidal $>$S$^+$–H fragment. These are now weaker than before, because the overlap between the interacting orbitals is smaller. The stabilizing interaction (2) is also further reduced because the energy difference of the orbitals involved is now larger. The resulting effect of the various possible interactions is now a very small stabilizing effect, as is shown by the small positive value of the $\pi$ overlap population of the $C_1$–S bond (Table 5). This stabilizing effect is slightly increased if the sulfur atom is slightly moved out of the plane defined by the carbon atoms in the negative direction of $\gamma$.

The major conclusion of the above analysis is that the interaction of $>$S$^+$–H and the allyl fragment favours slightly a pyramidal configuration at sulphur. However the overall effect of such interaction is very small. Rather, *pyramidality at sulphur is an intrinsic property of the* $>$S$^+$–H *fragment arising from the stabilizing interaction between the sulphur lone pair and the vacant antibonding MO's spanning the sulphur ligands as described in a recent work.*[14]

The $\pi$ orbital interactions occurring in thiabenzene are shown in Fig. 3. In the planar conformation, there are three interactions: interactions (1) and (2) between the sulphur lone pair and the $\pi$ occupied MO's of the pentadienyl anion are four-electron interactions and, therefore, destabilizing in nature, and interaction (3) between the sulphur lone pair and the highest unoccupied $\pi$ MO of the pentadienyl anion is a two-electron interaction and therefore stabilizing in nature. The latter interaction is even smaller than the stabilizing interaction (2) in the thiacyclobutadiene, because of the larger energy difference between the interacting orbitals. Therefore, in this molecular system, the four-electron destabilizing interactions dominate, as can be seen from the significant negative value of the $\pi$ overlap population of the $C_1$–S bond (Table 5). In other words, it can be said that this molecule is destabilized in a planar conformation, something which is in agreement with Hückel's rule.[15] The antiaromaticity of planar thiabenzene is reduced with pyramidalization at the sulphur center, mainly as a result of reduced destabilizing interactions: when the $>$S$^+$–H fragment is pyramidal, the overlap between the interacting orbitals is significantly reduced. Furthermore, the two-electron stabilizing interaction between the HOMO of the pentadienyl anion and the LUMO of the $>$S$^+$–H pyramidal fragment is now more significant than in the case of thiocyclobutadiene because the energy difference between the interacting orbitals is significantly smaller. Accordingly, the $C_1$–S $\pi$ overlap population has become positive, and also the total overlap population (which can be taken as a measure of the covalent character of the bond) is significantly larger. The computed value of the $C_1$–S bond distance (Table 4) is larger than in thiophene (Table 1), but significantly smaller than that for a single C–S bond.

In addition to reduction of $\pi$ "antiaromaticity" effected by pyramidalization, the intrinsic configurational preference of $>$S$^+$–H is also satisfied by this geometric change so that the effects work in the direction of producing an ylide-like structure in the case of thiabenzene. On the other hand the interaction between the pentadienyl anion and the $>$S$^+$–H fragment is responsible for the relative stability of the pyramidal conformations. Here, the most stable conformation should be the one which maximizes the dominant $\pi_3 - \phi_3$ interaction.

In summary, the most important conclusions of the present work are the following:

(a) Planar thiabenzene is destabilized as expected on the basis of Hückel's pi "aromaticity" rules. Also planar thiacyclobutadiene is destabilized, but only to a very small extent and in contrast to Hückel's rules. In this latter case, naive applications of the aforementioned rules would lead one to expect considerable stabilization. The "non-aromaticity" of thiacyclobutadiene has been traced to a large HOMO–LUMO energy gap of the component fragments.

(b) Both thiacyclobutadiene and thiabenzene contain pyramidal sulphur. In both cases, the two important electronic effects, i.e. the intrinsic preference of tricoordinate sulphur to adopt a pyramidal geometry and the pi interactions, work hand in hand to enforce a pyramidal geometry. However, the effect of the pi interactions is much more significant in thiabenzene than in thiacyclobutadiene.

(c) The magnitude of the energy gap between the fragment MO's whose interaction confers maximum stabilization to the total system can serve as an index of the degree of "aromaticity" or "antiaromaticity" of a heterocycle. For example, a large gap renders planar thiacyclobutadiene (Fig. 2) "non-aromatic" and planar thiabenzene (Fig. 3) appreciably "antiaromatic".

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