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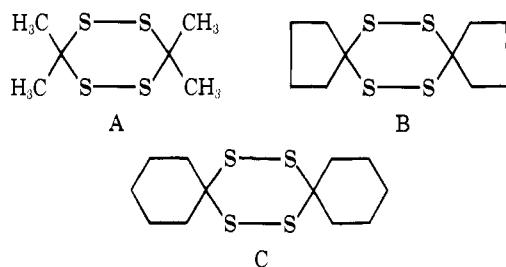
## Application of Photoelectron Spectroscopy to Conformational Analysis of *S*-Tetrathianes<sup>1</sup>

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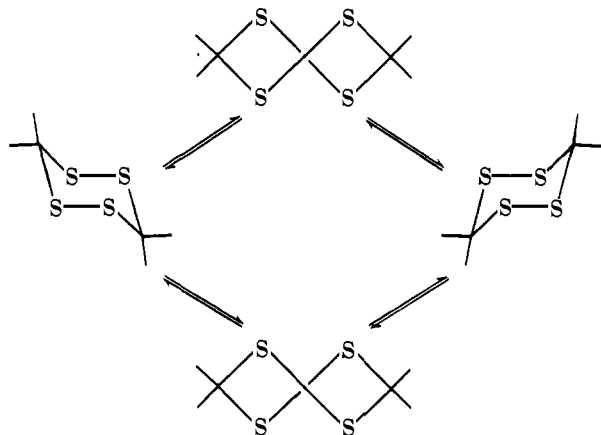
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**Abstract:** The conformational study of three *S*-tetrathianes has been accomplished by photoelectron spectroscopy. After evaluation of the magnitudes of the interactions between the sulfur lone pairs in the two probable forms of *S*-tetrathianes (chair and twist forms), we conclude that the preferential forms in the vapor phase are twist for 3,3,6,6-tetramethyl-*S*-tetrathiane, and chair for the 3,3:6,6-bis(tetramethylene) and 3,3:6,6-bis(pentamethylene) derivatives.

Many <sup>1</sup>H NMR studies have been reported concerning the three *S*-tetrathiane derivatives:<sup>2</sup> 3,3,6,6-tetramethyl-*S*-tetrathiane (A), 3,3:6,6-bis(tetramethylene)-*S*-tetrathiane (B), and 3,3:6,6-bis(pentamethylene)-*S*-tetrathiane (C).



For these three compounds, in solution in carbon disulfide, Bushweller et al.<sup>2</sup> concluded the existence of a chair to twist equilibration, the equilibrium ratio for each form being dependent on its substituents. However, recent x-ray crystallographic studies on tetrathianes have shown that 3,3,6,6-tetramethyl-*S*-tetrathiane<sup>3</sup> exists in the twist con-



formation and that 3,3:6,6-bis(pentamethylene)-*S*-tetrathiane<sup>21</sup> exists in the chair conformation in the crystal.

The purpose of our study has been to determine the preferential conformation of these compounds in the vapor

phase. We have already used photoelectron spectroscopy for a study of 1,2,4-trithiolane derivatives<sup>4,5</sup> and shown that this technique allowed us to determine directly the interactions between the lone pairs of heteroatoms. These interactions are dependent upon the conformations of the compounds studied.

The four highest occupied molecular orbitals of *S*-tetrathianes correspond to the lone pairs of sulfur atoms. The positions of the MO's of different symmetry are determined solely by the interactions between the lone pairs.<sup>6</sup> Therefore, we found it useful to make an initial estimate of the importance of these interactions for each conformer considered, before proceeding to analyze the experimental spectra.

### Analysis of the Interactions Involved

A priori, we can consider individually three kinds of interactions for each of the two conformers (chair and twist forms): 1-2, 1-3, 1-4 interactions (Figure 1).

**1-2 Interaction.** This "through-space" interaction has a clear dependence on the dihedral angle  $\theta$  defined by the directions of the lone pairs. The splitting into bonding ( $n_1 + n_2$ ) and antibonding ( $n_1 - n_2$ ) combinations ( $\Delta E_{1,2}$ ) that results from this interaction reaches a maximum for a  $\theta = 0^\circ$  and a minimum for  $\theta \sim 90^\circ$ .<sup>7-14</sup> For the chair form of 3,3:6,6-bis(pentamethylene)-*S*-tetrathiane, the angle  $\theta$  was reported to be  $66^\circ$  in the crystalline form.<sup>21</sup> This value corresponds to a  $\Delta E_{1,2}$  splitting of about 0.6-0.7 eV. For the twist form, we can expect a slightly larger  $\theta$  ( $\approx 80^\circ$ ) thus a slightly smaller splitting.

**1-3 Interaction.** When the molecule exists in a conformation with two nonparallel lone pairs separated by a tetragonal carbon (which occurs in the chair and twist conformers of *S*-tetrathiane) "through space" interaction (direct overlap) causes splitting into destabilized minus ( $n_1 - n_3$ ) and stabilized plus ( $n_1 + n_3$ ) combinations. The  $\Delta E_{1,3}$  splitting had been estimated to be 0.45 eV for 1,3-dithiane<sup>15</sup> and to be 1.07 eV for dimercaptomethane.<sup>16</sup> For *S*-tetrathiane, this interaction, which is very similar in both the chair and twist form, should produce a splitting between 0.5 and 1 eV.

**1-4 Interaction.** The nature and the importance of this interaction will, in contrast, be very different according to the conformer.

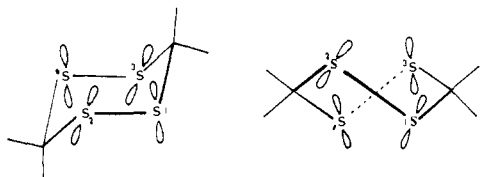


Figure 1. Sulfur lone pairs in chair and twist forms of *S*-tetrathiane.

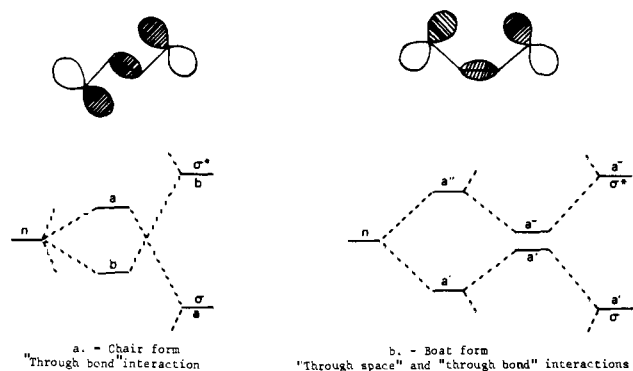


Figure 2. Qualitative MO scheme for  $n_s/n_s$  and  $n_s/\sigma$  interactions in 1,4-dithiane.

Let us consider the simple case of 1,4-dithiane. In the chair form, the direction of the lone pairs of  $S_1$  and  $S_4$  sulfur atoms is parallel and the "through space" interaction can be neglected. On the other hand, as Sweigart and Turner have showed for this compound as well as for 1,4-dioxane<sup>15</sup> (which both contain a symmetry axis passing through

the center of the C-C bonds), there occurs a destabilization of the minus ( $n_1 - n_4$ ) combination (symmetry a) by interaction with the  $\sigma_{C-C}$  bonding orbital of same symmetry and a stabilization of the plus ( $n_1 + n_4$ ) combination (antisymmetric with respect to the axis (symmetry b)) by interaction with the  $\sigma_{C-C}^*$  virtual orbital (Figure 2a).

If we consider a boat form of 1,4-dithiane with a sulfur atom at each prow position containing a symmetry plane bisecting the C-C bonds, the "through-space" interaction can no longer be neglected. This interaction leads to a destabilization of the minus combination of symmetry  $a''$  (antisymmetric with respect to the plane) and a stabilization of the plus combination (symmetry  $a'$ ). To this through space interaction, a "through bond" interaction with  $\sigma_{C-C}$  and  $\sigma_{C-C}^*$  orbitals<sup>17</sup> must be added, which destabilizes the bonding component and stabilizes the antibonding component (Figure 2b).

These results may be transposed to tetrathianes if we consider two "pseudoaxes" bisecting opposite C-S bonds in the chair form and two "pseudoplanes" bisecting these bonds in the twist form. The approximate symmetric interactions described lead to a  $\Delta E_{1,4}$  much smaller for the twist form than for the chair form (Figure 2).

The nature of these orbital interactions allows us to use the formalism of the perturbation method.<sup>18,19</sup> In second order, we can calculate the difference between the energy of the algebraic mean of the orbitals before and after perturbation. For two degenerate orbitals (lone pairs) this difference is proportional to the square of the overlap integral  $S^2$ <sup>20</sup> when we apply the approximation of Mulliken.<sup>21</sup> This

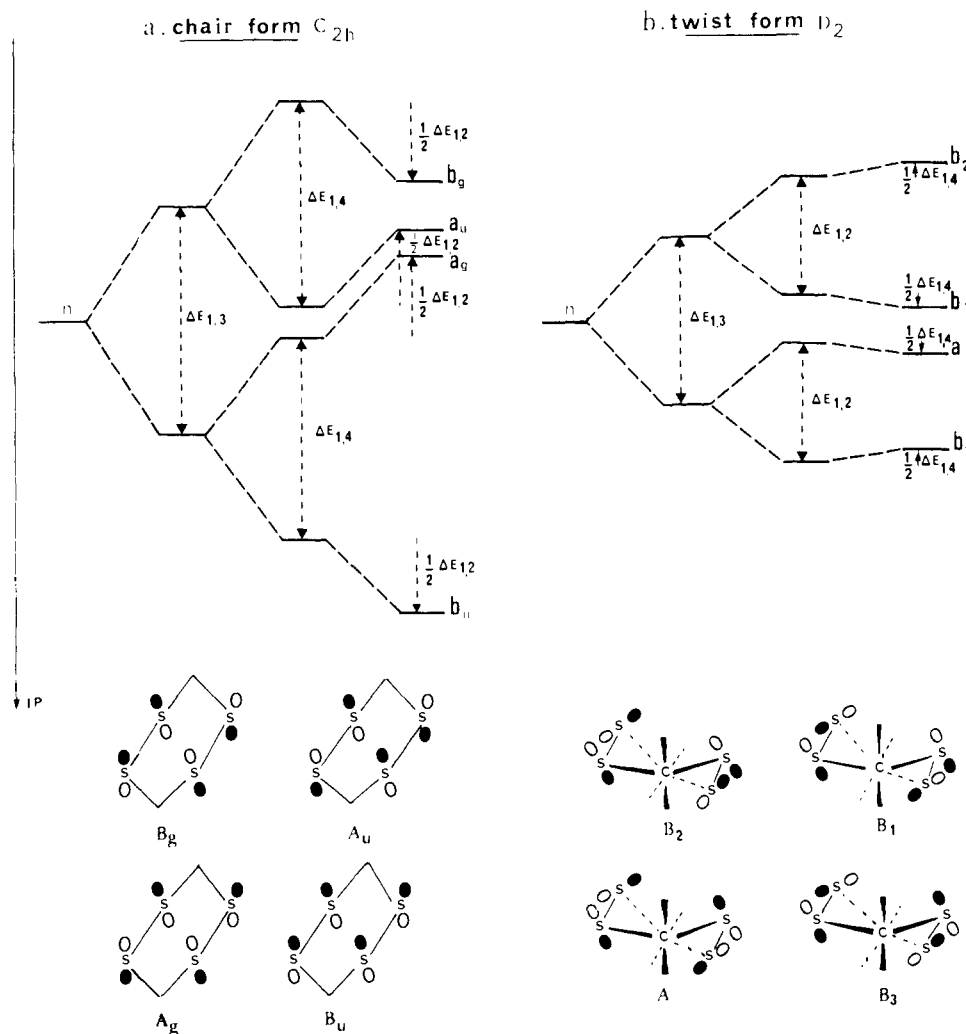


Figure 3. Qualitative MO scheme for  $n_s/n_s$  interaction in *S*-tetrathiane.

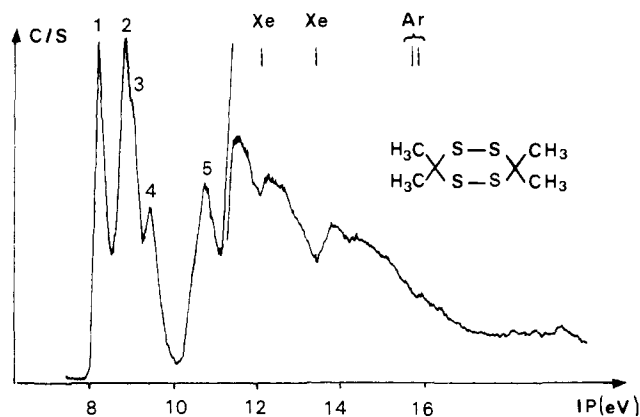


Figure 4. Photoelectron spectrum of 3,3,6,6-tetramethyl-*S*-tetrathiane (A).

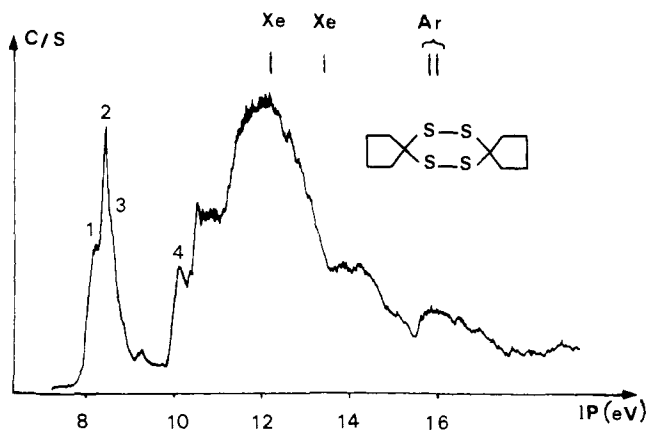


Figure 5. Photoelectron spectrum of 3,3,6,6-bis(tetramethylene)-*S*-tetrathiane (B).

integral is always smaller than 0.2, thus we can neglect  $S^2$  which must be less than 0.04.

In Figure 3, we have qualitatively visualized the superposition of the interactions above analyzed for the chair and the twist forms of *S*-tetrathiane, neglecting overlap. We have considered as a first approximation that the 1-2 and 1-3 interactions have similar values. The 1-4 interaction in the chair form has been estimated of similar importance since it is equal to 0.41 eV in 1,4-dithiane<sup>15</sup> and very small for the twist form.

#### Photoelectron Spectra of *S*-Tetrathianes

The spectra of the three compounds are presented in Figures 4, 5, and 6. The values of the corresponding vertical ionization potentials are presented in Table I. We notice a considerable difference in the shape and the position of the four first bands of the spectrum of 3,3,6,6-tetramethyl-*S*-tetrathiane (A) in comparison with the spectra of the two derivatives substituted by cyclic groups (B and C). For compound A (Figure 4) the difference between the two first ionization potentials is 0.62 eV and that between the third and fourth ionization potentials is 0.40 eV. For compounds B and C (Figures 5 and 6) the first difference is respectively 0.22 (B) and 0.36 eV (C); the second difference is 1.63 (B) and 1.5 eV (C).

If we compare these experimental data with the differences given by the qualitative interaction diagram (Figure 3)<sup>22</sup> we can conclude that A exists in a twist conformation while B and C are in a chair conformation. Nevertheless, we have observed a weak band at 9.22 eV in the spectrum of B which can be assigned to the fourth ionization potential of

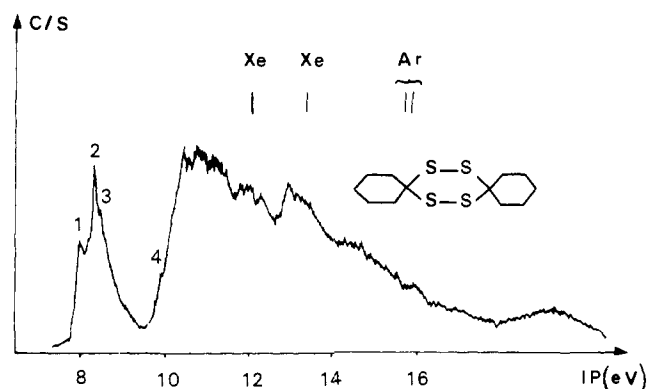


Figure 6. Photoelectron spectrum of 3,3,6,6-bis(pentamethylene)-*S*-tetrathiane (C).

Table I. Vertical Ionization Potentials (eV) of 3,3,6,6-Tetramethyl-*S*-tetrathiane (A), 3,3,6,6-Bis(tetramethylene)-*S*-tetrathiane (B), and 3,3,6,6-Bis(pentamethylene)-*S*-tetrathiane (C)<sup>a</sup>

A	B	C
8.23	8.17	7.98
8.85	8.39	8.34
9.04	8.4*	8.5*
	(9.22)	
9.44	10.03	10*

<sup>a</sup> These potentials are given with an accuracy of  $\pm 0.02$  eV except those with an asterisk which are given with a smaller precision because of the overlapping of the bands. The value in parentheses corresponds to the band assigned to the second form of the B compound.

the twist form which might exist in low ratio in the vapor phase.

From Figure 3 and the differences experimentally observed, we try to give a quantitative evaluation of the different interactions. There are six possible sets of assignments (3!), i.e., three values of  $\Delta E$  that correspond to each of the three interactions (1-2, 1-3, 1-4). However, it is possible to eliminate some of these solutions. For the twist form of 3,3,6,6-tetramethyl-*S*-tetrathiane the three values of  $\Delta E$  are 0.1, 0.5, and 0.7 eV. Since the smaller interactions must be  $\Delta E_{1,4}$  we assign the value 0.1 eV to  $\Delta E_{1,4}$ . For the dimercaptomethane, the 1-3 interaction results in a splitting of 1.07 eV.<sup>16</sup> If we assign the value 0.7 eV to this interaction for the twist form of *S*-tetrathiane, the interaction  $\Delta E_{1,2}$  would be 0.5 eV which would correspond to a dihedral  $\theta$  angle included between 70 and 75°. As expected this angle is slightly larger than that determined for the chair form of 3,3,6,6-bis(pentamethylene)-*S*-tetrathiane in the crystal ( $\theta = 66^\circ$  21). For the chair form (compounds B and C) the experimental values of splittings are very similar: 0.66, 0.85, and 0.95 eV for B and 0.57, 0.93, and 1.09 eV for C. The values 0.66 and 0.57 eV evidently correspond to an 1-2 interaction for a  $\theta$  angle of 66°. The other values are too similar to be assigned.

Finally we note that this interpretation is in perfect agreement with CNDO/S (the CNDO/S<sup>23</sup> method has been used because it generally gives results in good agreement with the experimental values<sup>24,25</sup>) calculations on the *S*-tetrathiane in the chair and twist forms (Table II). These calculations were performed using the structure given by Bushweller et al.<sup>21</sup> for the chair form and a geometry for the twist conformer that we constructed from the same bond distances and ring angles.

#### Conclusion

We conclude that in the vapor phase 3,3,6,6-tetramethyl-*S*-tetrathiane (A) and 3,3,6,6-bis(tetramethylene)-*S*-tetra-

**Table II.** CNDO/S Calculated Values (eV) of the Energies Associated with the Highest Occupied Molecular Orbitals (with Their Symmetries) for a Chair Form (Experimental Structure<sup>21</sup>) and for a Twist Form of *S*-Tetrathiane

Chair form ( $C_{2h}$ )	Twist form ( $D_2$ )
9.33 ( $a_g$ )	9.38 ( $b_2$ )
9.39 ( $b_g$ )	10.00 ( $b_1$ )
9.74 ( $a_u$ )	10.19 ( $a$ )
12.37 ( $b_u$ )	10.84 ( $b_3$ )

thiane (B) prefer respectively the twist and chair conformations. It is interesting to note that these two compounds present the same preferential structure in solution<sup>2</sup> (A: 70% twist form; B: 80% chair form at  $-15^\circ\text{C}$  in  $\text{CS}_2$ ) as in the crystal for compound A.<sup>3</sup> This is not the case for the 3,3:6,6-bis(pentamethylene) derivative (C) which exists in a chair conformation in the vapor phase as well as in the crystal<sup>21</sup> but prefers the twist form in solution (20% chair form at  $-15^\circ\text{C}$  in  $\text{CS}_2$ ).

### Experimental Section

In this study, we have used a Perkin-Elmer PS<sub>18</sub> photoelectron spectrometer with a flowing helium discharge lamp source (He(I), 584 Å). The resolution was at about 20 meV. The spectra were calibrated with <sup>2</sup>P<sub>1/2</sub> and <sup>2</sup>P<sub>3/2</sub> doublet of xenon (12.127 and 13.427 eV) and argon (15.755 and 15.943 eV).

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## Relationship between Orbital Ionization Energies and Molecular Properties. Proton Affinities and Photoelectron Spectra of Nitriles

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**Abstract:** Proton affinities are determined for a series of nitriles using ion cyclotron resonance techniques. Photoelectron spectra of nitriles are also obtained. In previously examined series of bases, linear relationships have been established between proton affinities and adiabatic first ionization potentials which correspond to removal of an electron from a lone pair localized at the site of protonation. Nitrile proton affinities are found to be linearly related not to the first CN  $\pi$  ionization potentials but rather to the adiabatic N lone pair  $\sigma$  ionization potentials at higher energy. This relationship provides a useful chemical means for the assignment of bands in photoelectron spectra; specific examples are considered and assigned. A linear relationship is also found between nitrile (RCN) and primary amine (RNH<sub>2</sub>) proton affinities for a range of substituents R. The results are discussed in terms of the intrinsic factors affecting molecular basicity.

Recent developments in techniques for the study of ion-molecule reactions have made it possible to quantify base strengths relative to a variety of cationic reference acids in the gas phase.<sup>2-13</sup> While Li<sup>+</sup>, K<sup>+</sup>, NO<sup>+</sup>, and other species are now also being studied,<sup>11-13</sup> the most widely studied reference acid has been the proton.<sup>2-10</sup> Proton affinity, PA(B),

is defined for a base B as the heterolytic bond dissociation energy for removing a proton from the conjugate acid BH<sup>+</sup>, eq 1. The homolytic bond dissociation energy  $D(\text{B}^+-\text{H})$  defined by eq 2 is related to PA(B) and the adiabatic ionization potentials IP(H) and IP(B), eq 3, by the thermochemical cycle 4.