# Rotational isomerism in tetramethyldistibane studied by UV photoelectron spectroscopy

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## Abstract

He(I) photoelectron spectroscopic (PE) measurements and ab initio calculations were performed on tetramethyldistibane. The spectroscopic measurements gave clear evidence for the existence of *gauche* and *anti* conformers in the gas phase. The composition of the rotameric mixture is 12% *gauche* and 88% *anti* conformers, estimated on the basis of the corresponding PE band areas. The Hartree–Fock calculations were performed using both effective core potential and all-electron 3–21 Gaussian basis sets. Full geometry optimizations were applied, resulting in theoretical evidence for the existence of the two rotamers. The calculated ionization energies seem to necessitate further studies on the assignment of the PE bands related to the antimony lone pairs.

*Keywords:* Antimony; Distibane; Photoelectron spectroscopy; Ab initio MO calculations; Gaussian calculations

## 1. Introduction

Tetramethyldistibane(I) is colorless in the gas phase, yellow as a liquid or in concentrated solutions, but bright red in the crystalline state [1,2]. In the solid state the distibane molecules adopt the *anti* conformation and are aligned to chains through short intermolecular contacts between the antimony atoms [3,4]. From vibrational spectra it has been concluded that both *gauche* and *anti* conformers are present in the liquid [5]. Equilibria between chains of oligomers have been made responsible for the hypsochromic shift of the absorption edge with lower concentrations of the solutions in benzene [6]. An investigation of the molecular structure by electron diffraction showed that the Sb–Sb bond length is shorter in the gas phase than in the solid state. The rotameric distribution and the complete geometries were, however, not determined [7]. As the conformational composition may have an influence on the colors in different phases, we were interested in a method to study the conformations in the gas phase also, and used He(I) ultraviolet photoelectron spectroscopy (UPS) and ab initio quantum–chemical calculations for this purpose. The UPS spectra of $Me_4P_2$ and $Me_4As_2$ have been reported [8].

## 2. Experimental

Tetramethyldistibane has been synthetized by reaction of $Me_2SbBr$ with Mg as described in the literature [9].

### 2.1. Photoelectron spectroscopy

He(I) photoelectron spectra were recorded on an ATOMKI ESA 32 instrument. The spectrometer, equipped with a hemispherical energy analyzer, has been described elsewhere [10]. During the measurements the energy resolution was smaller than 0.03 eV. The sample was introduced into the ionization chamber via a gas inlet system at room temperature. The spectra were calibrated using nitrogen and methyliodide as internal standards. Maximum errors in ionization energies are estimated at less than 0.05 eV. The data from 20–60 scans were accumulated by a PC.

### 2.2. Quantum–chemical calculations

Ab initio calculations were carried out on the title compound using both effective core potential and all-electron basis sets. For the ECP calculations Los Alamos metal core potentials and double zeta valence basis sets were used [11]. For the carbon and hydrogen atoms the

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full double zeta basis sets of Dunning and Hay [12] were applied. All-electron calculations were carried out using the 3–21G sets of Pople and coworkers [13–15] with diffuse or polarization functions. Full geometry optimizations were performed using the Gaussian 94 program system of Frisch et al. [16] on an IBM RS/6000 model 580 computer.

## 3. Results and discussion

The whole He(I) photoelectron (PE) spectrum and its low-energy part between 7.5 and 11 eV are shown in Figs. 1 and 2. In Fig. 2 a least-squares fit to experimental data and the deconvoluted spectrum are represented by solid lines. Vertical ionization energies (IE), together with those of tetramethyldiphosphine and -diarsine [8] and the first ionization energies of the corresponding trimethyl derivatives [17], are given in Table 1.

The PE spectra of $Me_4P_2$, $Me_4As_2$ and $Me_4Sb_2$—apart from different intensity relationships caused by different analyzer transmission characteristics—are extremely similar. That is why the interpretation of the spectrum is quite straightforward with the same reasoning as used by Cowley et al. [8] in the case of phosphorus and arsenic analogues. Namely, the second peak is obviously too small to be regarded as ionization from the same molecule; its presence requires the assumption that the compound is a mixture of rotamers in the gas phase. Accordingly, $IE_1$ and $IE_3$ can be assigned to the lone pairs of the *anti* rotamer, split by lone pair–lone pair (lp–lp) interaction, and $IE_2$ to the lone pairs of the *gauche* rotamer, where this interaction is virtually absent. $IE_4$ corresponds to the Sb–Sb bond while $IE_5$ and $IE_6$ are attributed to ionizations from Sb–C bonding orbitals. The average energy difference between analogous ionizations of the As and Sb compounds is 0.2–0.3 eV for $n_E$, 0.4 eV for E–E, and 0.55 eV for E–C, in good agreement with the trends observed for other pairs of As and Sb compounds [18].

Based on the above interpretation $IE_2$ can be related to an unperturbed heteroatom lone pair ionization, as far
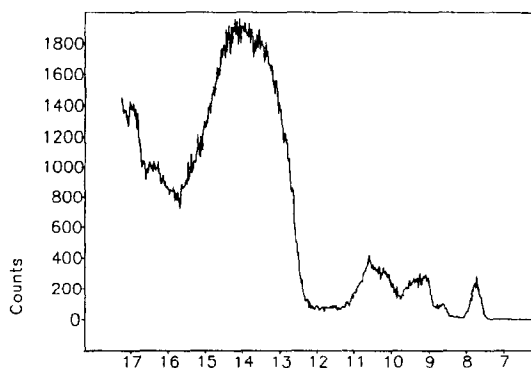


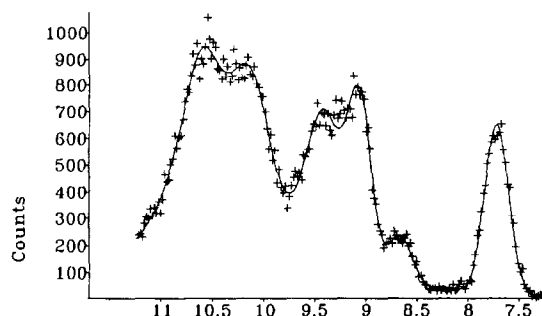Fig. 1. He(I) Photoelectron spectrum of $Me_4Sb_2$.



Fig. 2. Photoelectron spectrum of $Me_4Sb_2$ in the energy range 7.5–11 eV. Least-squares fit and the deconvoluted spectrum are represented by solid lines.

as lp–lp interaction is concerned. Consequently it can be compared with the first ionization energy of the corresponding trimethyl derivative. It is clearly seen from Table 1 that the $IE_2$ values of the tetramethyl compounds show the same trend as the $IE_1$s of the corresponding trimethyls. The ca. 0.2 eV stabilization can be ascribed to the smaller pyramidalization around the Sb atom as a result of the increased steric demand of the dimethylstibine group.

An alternative assignment attributing $IE_3$ to the Sb–Sb bond and $IE_4$ to the in-phase lone pair combination cannot be ruled out, but it is less likely because the sharp onset of the third band is rather typical of a lone-pair ionization while the fourth band looks more like a broad envelope characteristic of bonding orbitals. This alternative assignment, however, would place the Sb–Sb bond 0.76 eV above the As–As bond, which is closer to the value of approximately 0.9 eV observed for the Walsh-type orbitals of $As_3$- and $Sb_3$-substituted nortricyclanes [19].

The analysis of data summarized in Table 1 reveals further details. Namely, the average of $IE_1$ and $IE_3$ of tetramethyldiphosphine and -diarsine are respectively 0.08 and 0.15 eV less than the corresponding $IE_2$ values ($\Delta'$). This downward shift is ascribed to the destabilizing effect of *anti* lone pair interaction. In the case of tetramethyldistibane $\Delta'$ is equal to 0.27 eV, indicating a more significant lone pair repulsion. However, the splitting between $IE_1$ and $IE_3$ ($\Delta$) decreases on going down in the series, contradicting the above statement. The

Table 1
Vertical ionization energies (eV) and related data

| Compound | $IE_1$ | $IE_2$ | $IE_3$ | $IE_4$ | $IE_5$ | $IE_6$ | $\Delta$ (eV) [a] | $\Delta'$ (eV) [b] |
|---|---|---|---|---|---|---|---|---|
| $Me_4P_2$ [8] | 7.88 | 8.79 | 9.54 | 10.33 | 11.22 | 11.83 | 1.66 | 0.08 |
| $Me_4As_2$ [8] | 7.91 | 8.85 | 9.50 | 9.82 | 10.60 | 11.21 | 1.59 | 0.15 |
| $Me_4Sb_2$ | 7.72 | 8.66 | 9.06 | 9.42 | 10.12 | 10.60 | 1.34 | 0.27 |
| $Me_3P$ [17] | 8.60 | | | | | | | |
| $Me_3As$ [17] | 8.65 | | | | | | | |
| $Me_3Sb$ [17] | 8.48 | | | | | | | |

[a] $\Delta = IE_3 - IE_1$.
[b] $\Delta' = IE_2 - [(IE_1 + IE_3)/2]$.

Table 2

HF equilibrium geometries of $Me_4Sb_2$ in pm and degrees

| Basis set | r(Sb–Sb) | r(Sb–C) | ∠C–Sb–C | Torsion [a] |
|---|---|---|---|---|
| Gauche conformer | | | | |
| 3–21G | 293.9 | 218.7–218.8 | 95.48 | 66.84 |
| 3–21+G | 294.1 | 218.6 | 95.58 | 73.70 |
| 3–21G ** | 293.8 | 219.2–219.3 | 95.46 | 71.02 |
| LanL2dz (ECP) | 287.2 | 217.4–217.5 | 95.69 | 69.55 |
| | | | | |
| Anti conformer | | | | |
| 3–21G | 294.0 | 218.4–218.7 | 95.10 and 95.17 | 196.04 |
| 3–21+G | 293.9 | 218.6 | 95.48 | 188.03 |
| 3–21G ** | 293.8 | 219.2–219.3 | 95.07 | 194.48 |
| LanL2dz (ECP) | 287.5 | 217.6 | 95.43 | 180.00 |

[a] Me–Sb–Sb–Me torsion.

alternative assignment, i.e. accepting $IE_4$ as the bonding lone-pair combination, does not resolve this controversy either, since it would give a splitting of 1.70 eV accompanied by a net average anti-destabilization of only 0.09 eV.

We intended to find theoretical arguments also for the existence of the two rotamers, and to calculate ab initio geometries for them. We calculated ionization energies via Koopmans' theorem [20] and compared these with experimental ionization energies found in the photoelectron spectrum.

The geometry optimizations were successful in all cases, resulting in suitable geometries for both conformers. Some characteristic data of the equilibrium geometries are given in Table 2 (The complete calculated geometries can be obtained as supplementary material via www at http://www.chem.elte.hu/ General/ UPS/ distib.html.). The antimony–antimony distance was found to be between 287 and 294 pm in both conformations. The torsion angle of the Sb–Sb bond was defined as a methyl–Sb–Sb–methyl torsion. This angle was calculated to be between 180° and 190° in the
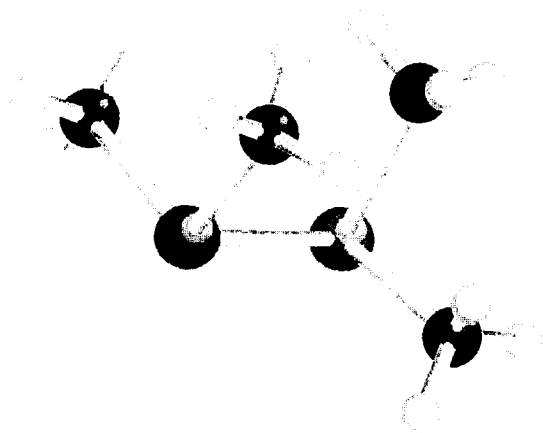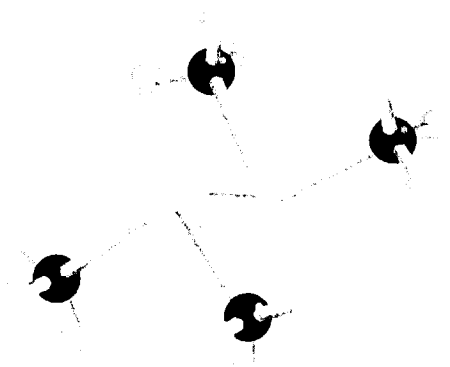


Fig. 4. Ab initio HF/3–21+G geometry of the anti conformer of $Me_4Sb_2$.

anti conformer and between 66° and 74° in the other case. In the all-electron calculations there were two minima on the potential energy curve at a few degrees above and below 180° with respect to the torsion coordinate. However, there should be only one anti conformer at this level of theory because of the very low activation barrier at 180°. The minimum was found to be almost exactly at 180° in the ECP calculation. The gauche and anti structures are shown in Figs. 3 and 4. Conformational ratios of the compound were not computed because the accuracy of the energy differences is not satisfactory at this level of theory.

The energies of the two highest molecular orbitals are given in Table 3. Interpreting these data via Koopmans' theorem gives an antimony lone-pair splitting of about 2.0 eV in the anti and about 1.2 eV in the gauche conformer. These results are not completely reliable because of the approximate nature of Koopmans' theorem, but they reveal an alternative interpretation: Sb lp–lp interaction may also occur in the gauche conformer, resulting in a symmetric combination with $IE_2$ and an antisymmetric combination with $IE_1$ hidden in the intense first band.

## 4. Conclusions

Both PE measurements and quantum–chemical calculations prove the existence of gauche and anti ro-



Fig. 3. Ab initio HF/3–21+G geometry of the gauche conformer of $Me_4Sb_2$.

Table 3

HF orbital energies of $Me_4Sb_2$ (eV)

| Basis set | Gauche conformer | | | Anti conformer | | |
|---|---|---|---|---|---|---|
| | $-\varepsilon_2$ | $-\varepsilon_1$ | lp-splitting | $-\varepsilon_2$ | $-\varepsilon_1$ | lp-splitting [a] |
| 3–21G | 8.704 | 7.559 | 1.145 | 9.305 | 7.349 | 1.956 |
| 3–21+G | 8.855 | 7.644 | 1.211 | 9.427 | 7.463 | 1.964 |
| 3–21G ** | 8.702 | 7.563 | 1.139 | 9.290 | 7.359 | 1.931 |
| LanL2dz (ECP) | 8.813 | 7.603 | 1.210 | 9.482 | 7.395 | 2.087 |

[a] lp-splitting = $\varepsilon_1 - \varepsilon_2$.

tamers of $Me_4Sb_2$ in the gas phase. Their abundance can be estimated from the fitted low-IE region of the spectrum (Fig. 2). This estimation is based on the validity of assignment similar to that of diphosphines and diarsines [8], that is the first and third bands can be related to the *anti* and the second one to the *gauche* conformer. Equal band areas of the first and third band were enforced by fixing all parameters of the former to the latter. According to the fit parameters, the intensity of the second band is 14% of the combined intensities of the first and third bands, giving a composition of the rotameric mixture as 12% *gauche* and 88% *anti*. Tetramethyldiarsine was estimated to have exactly the same rotameric composition. Still, the two results might not perfectly match each other because of different analyzer transmissions.

As far as spectrum assignment is concerned our results seem to be in good agreement with those of Cowley et al. [8]. However, the controversy related to the tendencies in $\Delta$ and $\Delta'$ (Table 1) can hardly be interpreted. The ab initio Hartree–Fock calculations cast a new light on the problem. The calculated energies of the two uppermost molecular orbitals show well-defined lone pair splittings in both *gauche* and *anti* conformers. Considering the spectrum, this possibility cannot be ruled out; the low-intensity band related to the antisymmetric combination of the antimony lone pairs in the *gauche* rotamer could be merged in the intense first band so far ascribed exclusively to the *anti* rotamer. This problem can be clarified by further PE investigations scrutinizing fine details in the first band and making further quantum–chemical calculations on the title compound using post-HF methods including electron propagator calculations of the ionization energies.

## Acknowledgments

## References

[1] F.A. Paneth, *Trans. Faraday Soc., 30* (1934) 179.
[2] F.A. Paneth and H. Loleit, *J. Chem. Soc.,* (1935) 366.
[3] A.J. Ashe III, E.G. Ludwig, Jr., J. Oleksyszyn and J.C. Huffman, *Organometallics, 3* (1984) 337.
[4] O. Mundt, H. Riffel, G. Becker and A. Simon, *Z. Naturforsch., 39b* (1984) 317.
[5] H.J. Breunig, V. Breunig-Lyriti and W. Fichtner, *Z. Anorg. Allg. Chem., 487* (1982) 111.
[6] H.J. Breunig, in S. Patai (ed.), *The chemistry of organic arsenic, antimony and bismuth compounds,* Wiley, Chichester, UK, 1994, p. 441.
[7] A.G. Császár, L. Hedberg, K. Hedberg, E.G. Ludwig, Jr. and A.J. Ashe, *Organometallics, 5* (1986) 2257.
[8] A.H. Cowley, M.J.S. Dewar, D.W. Goodman and M.C. Padolina, *J. Am. Chem. Soc., 96* (1974) 2648.
[9] H.J. Breunig, V. Breunig-Lyriti and T.P. Knobloch, *Chemiker-Ztg., 101* (1977) 399.
[10] B. Csákvári, A. Nagy, L. Zanathy and L. Szepes, *Magyar Kémiai Folyóirat, 98* (1992) 415.
[11] W.R. Wadt and P.J. Hay, *J. Chem. Phys., 82* (1985) 284.
[12] T.H. Dunning, Jr. and P.J. Hay, in H.F. Schaefer III (ed.), *Modern Theoretical Chemistry,* Plenum, New York, 1976, pp. 1–28.
[13] J.S. Binkley, J.A. Pople and W.J. Hehre, *J. Am. Chem. Soc., 102* (1980) 939.
[14] M.S. Gordon, J.S. Binkley, J.A. Pople, W.J. Pietro and W.J. Hehre, *J. Am. Chem. Soc., 104* (1982) 2797.
[15] W.J. Pietro, M.M. Francl, W.J. Hehre, D.J. Defrees, J.A. Pople and J.S. Binkley, *J. Am. Chem. Soc., 104* (1982) 5039.
[16] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson et al., *Gaussian 94 (Revision B.2),* Gaussian Inc., Pittsburgh, PA, 1995.
[17] S. Elbel, H. Bergmann and W. Ensslin, *J. Chem. Soc., Faraday Trans. 2, 70* (1974) 555.
[18] L. Szepes, A. Nagy and L. Zanathy, in S. Patai (ed.), *The chemistry of organic arsenic, antimony and bismuth compounds,* Wiley, Chichester, UK, 1994, Chapter 7.
[19] R. Gleiter, H. Köppel, P. Hoffmann, H.R. Schmidt and J. Ellermann, *Inorg. Chem., 24* (1985) 4020.
[20] T. Koopmans, *Physica, 1* (1934) 104.