

Structure and Photoelectron Spectrum of Tetramethyldiarsane

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Abstract: A systematic theoretical investigation of tetramethyldiarsane is presented to help understand its structure and photoelectron spectrum. Full potential energy curve along the C–As–As–C torsion was calculated at the Hartree–Fock (HF) level, and complete geometry optimizations were performed at HF, second-order Many-Body Perturbation Theory (MBPT(2)), and Coupled-Cluster Singles and Doubles (CCSD) levels of theory. Two conformers, *anti* and *gauche*, have been found in accordance with the experimental observations. The calculated geometries are in good agreement with the electron diffraction results. Ionization energies were computed by the Equation-of-Motion Coupled-Cluster (EOM-CC) method. The calculations predict a substantial lone-pair splitting for both conformers which contradicts the original assignment of the photoelectron spectrum by Cowley et al. According to the new assignment, the first and third bands belong to the lone pairs of the *anti* rotamer, the second band is attributed to the n_+ lone-pair combination in the *gauche* conformer, while the peak of the n_- combination is merged with the intense first band previously ascribed exclusively to the *anti* rotamer. The conformer ratios calculated from the present assignment of the photoelectron spectrum are in good agreement with the quantum-chemical results. Since our assignment contradicts the theoretical reasoning, which the original assignment was based on, a new explanation is presented. We find that the *s*-character of the lone-pair orbitals increases in the order of nitrogen, phosphorus, arsenic, and antimony which explains not only the increasing pyramidalization of the Me₂E moiety but also the increasing splitting of the energy of the lone-pair MOs.

Introduction

The lone-pair interaction plays an essential role in stabilizing the conformers of molecules containing N–N, P–P, As–As, and Sb–Sb bonds. With only a few exceptions acyclic hydrazines (N–N bond) preferably adopt the *gauche* conformation,¹ while both the *anti* and *gauche* conformers are stable for the heavier congeners.^{2–6} The so called “*gauche* effect”,¹ in the case of hydrazines, can be explained by the repulsion between the two nitrogen lone pairs; the overlap is zero if the two lone pairs are perpendicular to each other (90°), but, of course, repulsion of the substituents prevents this situation and in the equilibrium geometry the angle between the lone pairs will differ from 90°. Note, however, that the existence of the *anti* conformer in the case of the heavier congeners suggests that other than this simplified lone-pair interaction scheme might also be important.

Since ionization energy from the lone pairs is usually small, photoelectron spectroscopy (PES) is an excellent tool for investigating these lone-pair interactions.³ First, different interaction of the lone pairs means different splitting of their ionization energy (IE); in the limiting case of negligible (or even zero) interaction no splitting would be observable. The splitting is, therefore, a qualitative measure of the angle between the lone pairs. Second, the lone-pair interaction is presumably different in different conformers, and, therefore, separate bands

in the PE spectrum will appear. Their intensity ratio is a measure of the conformer ratio.

In the case of hydrazine and its substituted analogs the two bands with the lowest ionization energies can be assigned to the n_+ and n_- combinations of the nitrogen lone pairs.⁷ Since in the *gauche* conformer the overlap of the lone pairs is small, the splitting of these two bands is small (0.4 eV in the case of tetramethylhydrazine). Usually no bands associated with the *anti* conformer can be observed proving that, due to the strong “*gauche* effect”, only one conformer exists.¹ Going down the periodic table, the PE spectrum changes: in the case of tetramethyldiphosphane and -diarsane three peaks attributed to the lone-pair orbitals have been observed.³ Since it was already known that in the gas phase not only the *gauche* but also the *anti* conformer was present, Cowley et al.³ assigned the peaks I₁ and I₃ to the n_+ and n_- lone-pair combinations of the phosphorus and the arsenic atoms in the *anti* form and the small-intensity band I₂ to lone pairs of the *gauche* conformer. This assignment was derived from Dewar’s theory⁸ which is based on semiquantitative MO theory (originally derived for organic compounds). Straightforward application of these rules on these compounds tells us³ that (a) the lone-pair splitting should be much larger in the *anti* than in the *gauche* form and (b) the mean of the lone-pair ionization energy should be the same in both conformers. The latter assumption is based on the fact that this mean energy corresponds to the noninteracting situation and therefore depends on the type of the atom only. The former argument, i.e., the dependence of the splitting on the angle between the lone pairs, was also supported by semiempirical MINDO/2 calculations.³ Since the intensity of the I₁ and I₃ lines is much higher than that of I₂, the more stable conformer was predicted to be the *anti* form.

There are several arguments against the above assignment: first, the splitting is not zero in tetramethylhydrazine which is

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[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1997.

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a typical example of the *gauche* conformation. Second, in a recent paper on the PES of tetramethyldistibane⁶ we analyzed how the splittings and the mean of the ionization energies for the two conformers vary for the different compounds. This analysis gave a hint that the assignment of Cowley *et al.*³ might not apply for tetramethyldistibane and also raised questions concerning Cowley's assignment for the other compounds.

Correct assignment is, of course, necessary to determine the conformer ratio. In the case of tetramethyldiarsane there is a controversy in this respect. The conformer ratio has been obtained by three different experimental techniques: the electron diffraction experiment of Downs and co-workers⁵ gave a rotameric composition of 40% *anti* and 60% *gauche*; from vibrational studies Durig and Casper² predicted a 60% *anti*, 40% *gauche* ratio; the original interpretation of the photoelectron spectrum by Cowley *et al.*³ lead to an 88% *anti* and 12% *gauche* abundance.

To resolve all these uncertainties about structure and spectrum of tetramethyldiarsane, we have performed systematic theoretical investigations. As a first step, we calculated the equilibrium geometry and the relative stability of the two rotamers by *ab initio* methods, and then we determined the ionization energies by very accurate theoretical methods. Since the calculations lead to a new assignment of the photoelectron spectrum, we finally performed qualitative analysis on the lone pair interaction in tetramethylhydrazine, -diphosphane, -diarsane, and -distibane and gave a new explanation of the trends outlined above.

The calculation of ionization energies is a well-established field of quantum chemistry; various levels of quantum chemical methods give a powerful tool to qualitatively understand, assign, or even quantitatively characterize photoelectron spectra. The simplest level consists of the application of the MO theory: inspecting the shape of the MOs, the interaction of the lone-pairs can be deduced, and one can qualitatively predict the splitting in PES. On the second level, a first estimate of the ionization potentials can be obtained by the simple Koopmans' theorem.⁹ Finally, highly accurate *ab initio* calculations including electron correlation, such as the Equation of Motion Coupled-Cluster method for Ionization Potentials (EOMIP-CCSD)^{10,11} (for more details see below), can be used to obtain *quantitative* estimates of the ionization energies. Thus, quantum chemical methods combined with photoelectron spectroscopy seem to be excellent tools to solve the problems mentioned above.

Computational Details

The calculations on the ground state have been performed at the restricted Hartree–Fock level. In order to include the effect of electron correlation, second-order Many-Body Perturbation Theory (MBPT(2), also referred to as MP2) and accurate Coupled-Cluster Singles and Doubles (CCSD) calculations were carried out. The CCSD calculations were performed with the ACESII¹² program package, while for the HF and second-order calculations Biosym's Turbomole v235¹³ and the Gaussian 94¹⁴ packages were used.

As already noted, *ab initio* calculation of the ionization energies can be performed at several levels. According to Koopmans' theorem,⁹ the ionization energies are given by the orbital energies from simple Hartree–Fock calculations. If orbital relaxation and correlation effects are important, higher level calculations are necessary for adequate accuracy. In this work we used the EOMIP-CCSD (Equation-of-Motion Ionization Potential Coupled-Cluster Singles and Doubles), also known

as CCGF (Coupled-Cluster Green's Function) method.^{10,11} The relation of this method to the better-known OVGf (Outer Valence Green's Function) method¹⁵ (which has been applied to several molecules¹⁶) was discussed by Nooijen and Snijders.¹⁷ Here we just mention that the necessary infinite order summation is performed in OVGf by solving the so-called Dyson's equation, while in EOMIP-CCSD the coupled-cluster equations are used. An advantage of the latter procedure¹⁷ is that it is not necessary to include the electron attached states in the calculation, which results in substantial savings in the computational requirements. The method has been shown to provide very accurate ionization potentials.¹⁰ It is, however, more expensive than the OVGf method since perturbational truncation is not involved. A second-order approximation (EOMIP-CCSD(2) or EOMIP-MBPT(2) or MBPT(2)-GF) has been proposed and tested.^{18,19} It was shown that the approximation does not introduce substantial error into the calculated IEs, but it is somewhat less expensive than the OVGf method. Finally, we mention that the close relationship of the EOMIP-CC methods to traditional quantum chemical approaches allows the derivation of analytical energy gradients, and, therefore, equilibrium geometry, vibrational frequencies, and other properties can be calculated for any of the ionized states.¹¹ In this work we have used the EOMIP-CCSD and EOMIP-CCSD(2) methods as implemented in a local version of ACESII²⁰ to calculate ionization potentials.

The quality of the basis sets is crucial for *ab initio* calculations. Correlated calculations require basis sets of at least double- ζ quality. On the other hand, the cost of the calculations, especially of the correlated ones, depends strongly on basis set size. We have performed calculations with several basis sets to get a handle on basis set effects: the 3-21G^{21,22} and 6-311G^{23,24} basis sets of Pople *et al.* with and without polarization functions and the double- ζ basis with polarization function (DZP) set of Ahlrichs and co-workers²⁵ were applied. We have also considered two types of basis set size reduction. First, by using pseudopotentials on the arsenic atoms, the number of electrons can be highly reduced. We have applied the effective core potentials of Hay and Wadt²⁶ with polarized double- ζ valence basis functions. As one may conclude from Tables 1 and 2, there is an insignificant change in geometry parameters when applying pseudopotentials in the basis set at both Hartree–Fock and second-order levels. Thus, the accuracy of the calculations is not influenced by the use of pseudopotentials. Secondly, we have also investigated the effect of polarization functions on the hydrogen atoms and found that the calculated geometries, conformer ratios, and lone-pair orbital energies changed only slightly when these functions were omitted. For all of these reasons, the most expensive coupled-cluster calculations were performed with ECP/dzp basis on arsenic, dzp on carbon, and dz on hydrogen atoms.

Results and Discussion

Rotamers and their Geometry. Both photoelectron spectroscopy³ and gas-phase electron diffraction measurements² have

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Table 1. Ab Initio Geometry of the Anti Conformer of Me₄As₂

level of theory	basis set	<i>r</i> (As–As)	<i>r</i> (As–C)	<i>r</i> (C–H)	∠(As–As–C)	∠(C–As–C)
HF	3-21G	253.2	198.0	108.3	96.88	97.43
	3-21G**	253.1	198.3	108.1	96.97	97.51
	6-311G	248.6	197.2	108.0	97.62	97.95
	6-311G**	245.0	197.4	108.4	97.83	97.97
	dzp	245.1	197.3	108.9	97.57	97.83
	ECP/dzp	243.9	196.9	108.9	97.48	97.66
	ECP/dzp (-H pol.) ^a	243.8	197.2	109.0	97.37	97.39
MBPT(2)	3-21G	256.1	199.2	109.5	95.98	96.62
	dzp	243.6	197.4	109.7	95.75	96.35
	ECP/dzp	243.8	197.4	109.8	95.46	96.10
	ECP/dzp (-H pol.) ^a	243.8	197.6	110.1	95.62	96.19
	ECP/dzp (-H pol.) ^a	245.5	198.3	110.4	95.82	96.22
CCSD	ECP/dzp (-H pol.) ^a	245.5	198.3	110.4	95.82	96.22
electron diffraction results ^{b,c}		243.3 (0.2)	197.3 (0.2)	111 ^d	95.4 (0.5)	95.3 (1.1)

^a ECP/dzp on As, dzp on C, dz on H. ^b From ref 5. ^c Figures in parentheses are the estimated standard deviations. ^d Fixed.

Table 2. Ab Initio Geometry of the Gauche Conformer of Me₄As₂

level of theory	basis set	<i>r</i> (As–As)	<i>r</i> (As–C)	<i>r</i> (C–H)	∠(As–As–C)	∠(C–As–C)	C–As–As–C torsion
HF	3-21G	253.5	197.9, 198.0	108.3	97.16, 101.49	98.07	70.24
	3-21G**	253.4	198.2, 198.3	108.1	97.26, 101.71	98.14	72.36
	6-311G	248.3	197.1, 197.2	108.0	97.89, 103.34	98.44	72.58
	6-311G**	244.7	197.2, 197.3	108.4	98.13, 103.75	98.50	76.55
	dzp	244.8	197.2	108.9	97.89, 103.60	98.42	77.07
	ECP/dzp	243.8	196.7	108.9	97.80, 103.65	98.29	76.52
	ECP/dzp (-H pol.) ^a	243.7	197.0	108.9	97.71, 103.45	97.99	75.53
MBPT(2)	3-21G	257.2	199.2, 199.3	109.5	96.03, 99.76	97.18	66.94
	dzp	243.7	197.1, 197.2	109.8	96.03, 101.78	96.87	73.72
	ECP/dzp	244.3	197.1, 197.2	109.8	95.74, 101.51	96.58	72.65
	ECP/dzp (-H pol.) ^a	244.3	197.5	110.1	95.95, 101.74	96.65	72.43
	ECP/dzp (-H pol.) ^a	246.1	198.1	110.4	96.12, 101.75	96.67	72.73
CCSD	ECP/dzp (-H pol.) ^a	246.1	198.1	110.4	96.12, 101.75	96.67	72.73
electron diffraction results ^{b,c}		243.3 (0.2)	197.3 (0.2)	111 ^d	95.4 (0.5)	95.3 (101)	90.5 (3.5)

^a ECP/dzp on As, dzp on C, dz on H. ^b From ref 5. ^c Figures in parentheses are the estimated standard deviations. ^d Fixed.

predicted the existence of two rotamers of Me₄As₂; their estimated ratio and even the relative stability of the conformers differed, however, significantly. In such cases theoretical predictions are of great importance. To that end, we first performed calculations on the geometry of both forms. We have used several levels of ab initio methods together with different basis sets. The results are summarized in Table 1 for the *anti* and in Table 2 for the *gauche* conformer. The calculations were performed utilizing the symmetry of the molecules, namely C_{2h} in the previous and C₂ in the latter case. This premise was sufficiently backed up by the experimental studies and proved by the absence of imaginary frequencies at the HF/ECP-dzp level.

In the following we compare our results on geometry to the experimental (ED) ones. Note that the experimental values refer to r_g structures, while the theoretical ones are equilibrium (r_e) values. This difference, however, does not influence the conclusions. The As–As and As–C bond lengths from the HF calculation with small basis sets are obviously overestimated. These bonds are calculated to be shorter at higher levels. The CCSD bond lengths are somewhat longer than the experimental values showing some missing effects from basis set. Consequently, considering error compensation, the MBPT(2)/dzp geometry is our best theoretical estimate.

During the refinement of the molecular structure in the electron diffraction study⁵ the As–As bond lengths were assumed to be identical in the two rotamers. According to the calculations, this assumption is reasonable indeed since the difference between the As–As bond lengths in the two conformers was found to be less than the estimated error of the calculated values. The theoretical As–C distances are in good agreement with the experimental results. The C–H bond length was fixed at 111 pm during the evaluation of the electron

diffraction data,⁵ which is just slightly longer than the computed values of 109–110 pm.

The pyramidalization of the AsMe₂ moiety in the molecule is of high interest: going down the periodic table the bond angles decrease. Comparing the bond angles in similar molecules containing atoms from a given column can give us some insight into the nature of chemical bonding in organoelement compounds and a prospect to understand the differences between classical organic and organoelement chemistry. Since the experimental determination of this quantity is difficult, calculations are of high importance. Again, in the electron diffraction study a constraint was necessary:⁵ the As–As–C and C–As–C angles in the *anti* and *gauche* conformers were fixed at the same value. While the calculated values for the *anti* conformer are in excellent agreement with the experiment, there is an important disagreement in the case of the *gauche* conformer: due to the reduced symmetry, the two As–As–C angles are not equivalent, and we find a large (about 5°) difference between them almost independently from the method used. On the other hand, the difference between the calculated and the measured C–As–C angles are close in the two conformers. The actual values of these angles confirm the increase of pyramidalization compared to the lighter congeners of Me₄As₂ as it will be discussed later in more detail.

The value of the C–As–As–C dihedral angle is a characteristic of the *gauche* conformer. In the electron diffraction experiment⁵ the dihedral angle can be estimated from the scattering corresponding to nonbonding C···C terms. The uncertainty of these data is quite large because their contribution to the total scattering is relatively small. The radial distribution curve is expected to show three distinct vicinal C···C distances ascribed to the *gauche* rotamer. The contribution of these is augmented by the similar C···C distances of the *anti* conformer

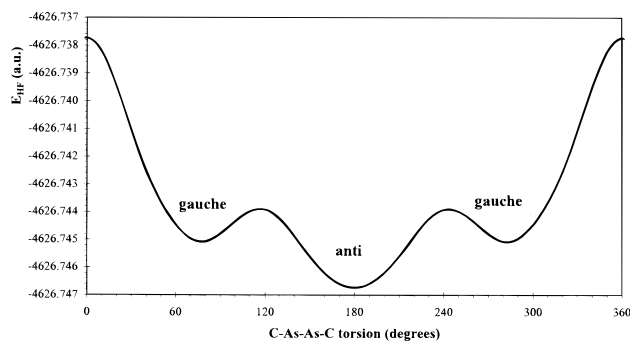


Figure 1. Potential energy curve of Me_4As_2 calculated at the HF/dzp level.

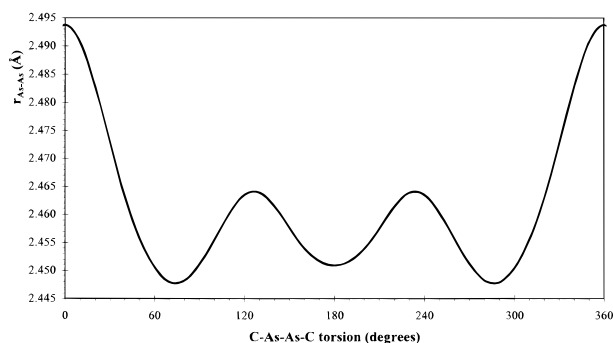


Figure 2. The dependence of the As-As distance on the C-As-As-C torsion.

and by those of numerous As \cdots H and C \cdots H distances resulting in a complicated pattern of the radial distribution curve, and, therefore, the estimation of the C-As-As-C dihedral angle is rather difficult. For this reason in the electron-diffraction studies of Me_4Sb_2 ,⁴ the heavier congener of Me_4As_2 , this torsion angle was kept fixed during the refinement of the structure. Downs *et al.*,⁵ on the other hand, chose to include the torsion angle in the refinement of the structure of Me_4As_2 . The obtained value of 90.5° differs considerably from the theoretical estimate of about 73° . Although the results of the calculations might be biased by deficiencies of the basis sets, the calculated dihedral angle is probably more reliable than the experimental one.

Figure 1 shows the potential energy curve along the C-As-As-C torsion calculated at the HF/dzp level. The three minima on the curve can be attributed to the *gauche*⁺, *anti*, and the *gauche*⁻ conformers with the *anti* (180°) being the absolute minimum. The shape of the calculated potential energy curve can be explained by lone pair-lone pair repulsion. At 180° , where the lone-pair orbitals are in *anti-periplanar* position, the largest interaction is possible. The other local minimum at about 77° corresponds to the *gauche* conformer. It indicates relative stabilization when the lone pairs are in *syn-clinal* position. The absolute maximum on this potential energy curve is at 0° where the repulsive interaction of the lone-pair orbitals is the highest.

The importance of the lone pair-lone pair repulsion can hardly be overemphasized. Another aspect of its importance is shown in Figure 2 where the dependence of the As-As distance on the torsion angle is plotted. It is clearly seen that the bond is shortest at the stable conformations. (Note that the correlated calculation predicts the As-As bond length slightly shorter in the *anti* form, while the HF/dzp level used here gives the opposite order. The difference is, however, insignificant.) The repulsion between the interacting lone pairs stretches the As-As bond causing significant destabilization of the molecule.

The Photoelectron Spectrum. As mentioned in the Introduction, quantum chemical methods can be used at three different levels to interpret photoelectron spectra. The first level,

Table 3. Ionization Energies of the Two Conformers Obtained Using Koopmans' Theorem

basis set	anti conformer			gauche conformer		
	IE ₁	IE ₂	ΔIE^a	IE ₁	IE ₂	ΔIE^a
3-21G	7.78	9.94	2.16	8.07	9.12	1.06
3-21G**	7.78	9.93	2.15	8.07	9.11	1.04
6-311G	7.94	10.10	2.16	8.27	9.23	0.96
6-311G**	7.91	10.05	2.14	8.24	9.16	0.93
dzp	7.92	10.06	2.14	8.16	9.13	0.97
ECP/dzp	7.94	10.12	2.18	8.24	9.22	0.98
ECP/dzp (-H pol.)	7.99	10.17	2.18	8.30	9.27	0.97
experimental ^b	7.91	9.50	1.59	8.85	8.85	

^a $\Delta\text{IE} = \text{IE}_2 - \text{IE}_1$. ^b From ref 3 (original assignment).

i.e., qualitative MO theory, states the following: the HOMO (Highest Occupied MO) of tetramethyldiarsane is the antibonding combination of the lone pairs (symmetry is A_g in the *anti* and A in the *gauche* conformer). The orbital with the second highest eigenvalue corresponds to the bonding combination (symmetry is B_u and B, respectively). These orbitals are shown in Figure 3. The splitting between these two levels will depend on the interaction of the individual lone pairs. The argument used by Cowley *et al.*³ to assign the spectrum was that splitting occurs in the case of the *anti* form since the lone pairs are in *anti-periplanar* position, while no splitting is assumed in the *gauche* form where the lone-pair orbitals are almost perpendicular to each other. The validity of this assumption will be discussed later.

The first estimate of the ionization energy is given by Koopmans' theorem.⁹ In Table 3 we list these values calculated with different basis sets. The orbitals corresponding to the lowest two ionization potentials are, as expected, best characterized as lone pairs of the arsenic atoms. In contrast to Cowley's³ assignment, there is a splitting in the IEs for both conformers: the splitting is larger in the *anti* form but clearly not negligible for the *gauche* form either. Comparing the calculated IEs of the *anti* conformer with the experiment, we find good agreement in the case of the first ionization energy, while the calculated value of the second IE is too high. Consequently, the calculated lone-pair splitting of 2.2 eV is about 0.6 eV larger than the experimental one. The first IE obtained for the *gauche* conformer is significantly lower than the value given by the original assignment of the PE spectrum. The second IE is much closer to this experimental value. The calculated lone-pair splitting in this conformer is about 1.0 eV, which is clearly not negligible.

Since this latter finding contradicts to Cowley's³ assumption of zero splitting, we have calculated the dependence of the lone-pair interactions on the C-As-As-C torsion angle at the HF/dzp level of theory in order to get a better understanding of the problem. As Figure 4 shows, the lone-pair splitting is the largest at $\theta = 180^\circ$, i.e., in the *anti* conformer, while the splitting is almost absent at $\theta = 0^\circ$. In the *gauche* conformer, which is characterized by a torsion angle of $\theta = 72-73^\circ$, the splitting is still significant. Cowley's prediction that there is no splitting in the case of the *gauche* form is based on the assumption that the lone-pair orbital energies coincide at 90° . The results displayed on Figure 4 clearly contradicts this assumption since they show that the interaction is still substantial when the lone pairs are almost perpendicular to each other. A qualitative explanation of this interaction will be presented below.

Both the Koopmans' IEs and the above analysis suggest a new assignment: the first and the third bands can be assigned to the lone pairs of the *anti* rotamer. The second band is attributed to the n_+ lone-pair combination in the *gauche*

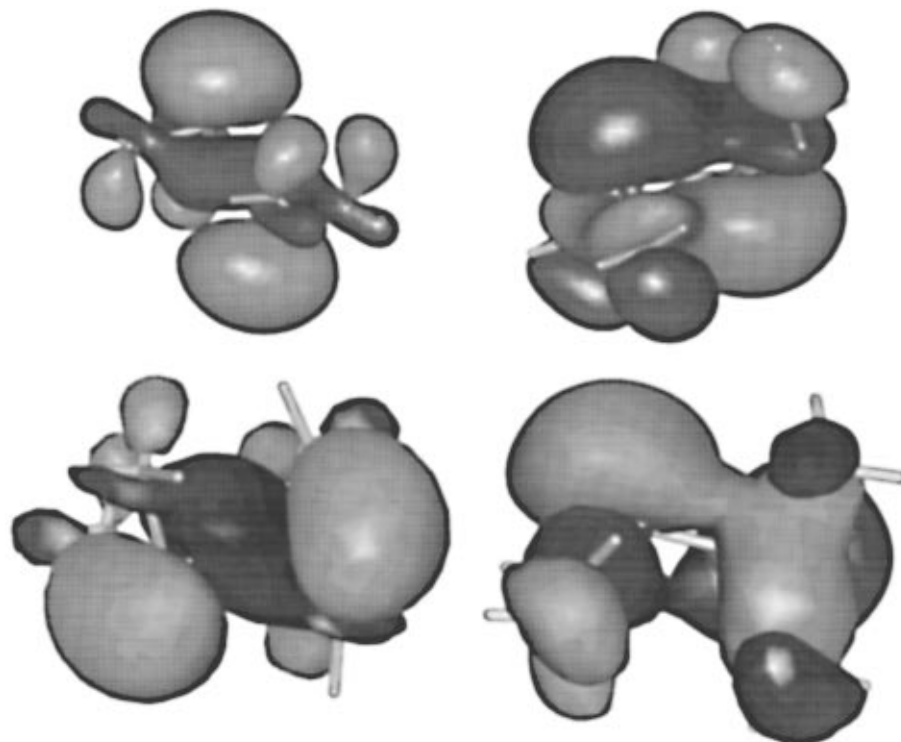


Figure 3. The lone-pair molecular orbitals of the gauche and anti form of Me_4As_2 : (a, top left) the antibonding combination of the arsenic lone pairs in the anti conformer, (b, top right) the bonding combination of the arsenic lone pairs in the anti conformer, (c, bottom, left) the antibonding combination of the arsenic lone pairs in the gauche conformer, and (d, bottom right) the bonding combination of the arsenic lone pairs in the gauche conformer.

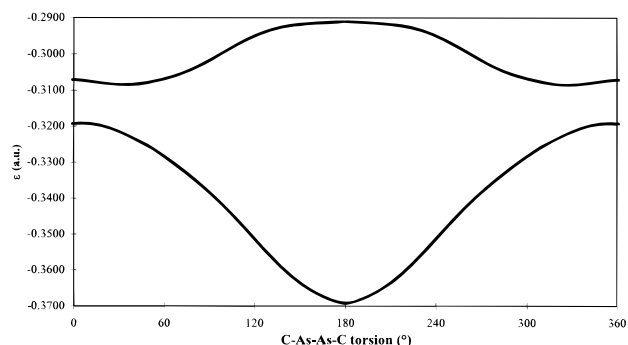


Figure 4. Orbital energies of the lone pair MO combinations as a function of the C–As–As–C torsion.

conformer, while the peak of the n_- combination is merged with the intense first band previously ascribed exclusively to the *anti* rotamer. This assignment gives a lone pair–lone pair splitting in the *gauche* conformer of about 0.8 eV. This assignment is in line with the one given by Schweig and co-workers²⁷ for the PE spectra of Me_4P_2 .

To support this idea, we went to the third level of quantum chemical treatment of the PE spectrum and performed very accurate calculation of the IEs by the EOMIP-CCSD method. As mentioned in the computational details, this method has an accuracy of about 0.1–0.2 eV for valence IEs; results are shown in Table 4. The lone-pair splitting in the *anti* conformer was calculated to be 1.72 eV, which differs by only 0.12 eV from the experimental value. In the case of the *gauche* conformer the calculated splitting is 0.75 eV. This result does not support the original assignment;³ however, the experimental lone-pair splitting of 0.85 eV based on the new interpretation above is in good agreement with the calculated value. As of the values of

the individual IEs, very good agreement with the experimental data was found: the average difference between the experimental and the calculated values is only 0.17 eV with the largest error being smaller than 0.25 eV. Therefore, one can be quite confident about the validity of our new assignment. The much less expensive EOMIP-CCSD(2) results are also given in Table 4. One can find that all IEs are within 0.1 eV relative to the full EOMIP-CCSD results.

Qualitative Model. In the light of the above reasoning, Dewar's theory for organic molecules⁸ used by Cowley et al.³ to interpret the spectrum seems not to be applicable to Me_4As_2 . Thus, a more satisfactory explanation is required. For this reason we return to the first level of quantum chemical treatment and analyze the composition of the lone-pair orbitals and its change with the increasing size of the central atoms. In the case of tetramethylhydrazine the overlap—and thus the interaction—of the nitrogen lone pairs is minimized at $\theta = 90^\circ$. This is the main source of the so-called “*gauche effect*”.

Why does this picture change in the case of the heavier congeners? The lone pairs of the nitrogen atoms are mainly p-type MOs. The overlap between two perpendicular p-type orbitals is clearly absent. Qualitative arguments suggest that the lone-pair orbitals in organoelement compounds of phosphorus, arsenic, and antimony have more s character.²⁸ In Table 5 the s-orbital contribution of the lone-pair orbitals are listed as obtained from population analysis of the HF/dz wave function. These data clearly support this qualitative picture: the s-orbital contribution to the n_+ lone pair combination is nearly zero in tetramethylhydrazine, and it monotonously increases from N to Sb, reaching almost 20% in tetramethyl-distibane. For lone pairs with substantial s character, the overlap would not vanish when the dihedral angle is approaching 90° .

(27) Schweig, A.; Thon, N.; Vermeer, H. *J. Am. Chem. Soc.* **1979**, *101*, 80.

(28) Szepes, L.; Nagy, A.; Zanathy, L. *The chemistry of organic arsenic, antimony and bismuth compounds*; Patai, S., Ed.; Wiley: Chichester, UK, 1994; pp 276.

Table 4. Ionization Energies at EOMIP-CCSD(2) and EOMIP-CCSD Levels of Theory

level of theory	basis set	anti conformer			gauche conformer		
		IE ₁	IE ₂	ΔIE ^a	IE ₁	IE ₂	ΔIE ^a
EOMIP-CCSD(2)	ECP/dzp (-H pol.)	7.572	9.303	1.731	7.785	8.561	0.777
EOMIP-CCSD	ECP/dzp (-H pol.)	7.644	9.354	1.710	7.855	8.600	0.744
	ECP/dzp	7.670	9.387	1.717	7.885	8.633	0.747
Experimental	original assignment ^b	7.91	9.50	1.59	8.85	8.85	
	present assignment	7.91	9.50	1.59	8.0	8.85	0.85

^a ΔIE = IE₂ - IE₁. ^b From ref 3.**Table 5.** The Effect of s-Orbital Contribution on the Pyramidalization and the lp-lp Splitting in the Gauche Conformer of Me₄E₂ (E = N, P, As, Sb)

	Me ₄ N ₂	Me ₄ P ₂	Me ₄ As ₂	Me ₄ Sb ₂
s-Orbital Contribution ^{a,b}				
A symmetry	2.0%	4.9%	4.7%	6.1%
B symmetry	3.5%	15.9%	16.4%	19.7%
Pyramidalization ^b				
E-E-C ₁ ∠	112.78°	98.79°	97.62°	95.90°
E-E-C ₂ ∠	116.84°	104.45°	102.70°	99.05°
C-E-C∠	115.85°	99.93°	98.28°	95.61°
Lone-Pair Splittings ^c				
IE ₁ (eV)	8.43 ^d	8.13 ^e	8.0 ^f	7.6 ^g
IE ₂ (eV)	8.83 ^d	8.75 ^e	8.85 ^h	8.66 ^h
Δ(IE)	0.40	0.62	0.8	1

^a s-Orbital contribution to the E lone-pair MOs. ^b Calculated at the HF/dz level of theory. ^c Δ = IE₂ - IE₁. ^d From ref 7. ^e From ref 26. ^f Estimated from the shape of the first band in the photoelectron spectra. ^g From ref 3. ^h From ref 6.**Table 6.** Rotameric Composition Obtained from the Differences of the Conformer Energies

level of theory	basis set	ΔE ^a (kJ/mol)	gauche (%)	anti (%)
HF	3-21G	5.27	19	81
	3-21G**	5.47	18	82
	6-311G	4.21	27	73
	6-311G**	4.17	27	73
	dzp	4.33	26	74
	ECP/dzp	4.61	24	76
	ECP/dzp (-H pol.)	4.27	26	74
	MBPT(2)	3-21G	4.32	26
dzp		4.20	27	73
ECP/dzp		4.73	23	77
ECP/dzp (-H pol.)		4.96	21	79
CCSD		ECP/dzp (-H pol.)	4.79	22

^a ΔE = E(gauche) - E(anti).

Consequently the lone-pair interaction will not vanish in the *gauche* conformer either and there will be a splitting of the corresponding IEs. Parallel to the increasing s character, the lone-pair splitting in the *gauche* conformer monotonically increases from tetramethylhydrazine to tetramethyldistibane.

The increasing s character has an interesting effect on the pyramidalization of the Me₂E moieties as well: due to the larger steric demand of the partially s-type lone pairs, the Me-E-Me and the Me-E-E angles decrease. Table 5 clearly shows the correlation among the lone pair s-character, the pyramidalization, and the lone pair-lone pair splitting.

Conformer Ratio. Since the conformer ratio obtained from the PE spectrum depends on the assignment, its value in tetramethyldiarsane has been calculated using several basis sets at HF, MBPT(2), and CCSD levels of theory. Table 6 shows the calculated energy difference between the two rotamers and the corresponding abundance ratio obtained using a simple Boltzmann distribution. Zero-point vibration effects are not included in these figures, but our calculation at the HF/ECP-dzp level of theory showed that it is negligible in this case.

The calculations predict that the *gauche* form amounts to about 21–27% in the gas phase. In comparison with various experimentally obtained ratios, the calculated value is in best agreement with the one derived from the new assignment of the PE spectrum (about 75% *anti* and 25% *gauche*). Since the ratio obtained using the old assignment is different (about 88% *anti* and 12% *gauche*³), we have an independent proof for our assignment. As far as the other two experimental values concerned, one can conclude that the prediction of *Durig* and *Casper*² (60% *anti*, 40% *gauche*) is qualitatively correct (i.e., the *anti* form is predicted to be more stable), while the results of *Downs* and co-workers⁵ seem to be incorrect even in the respect of relative stabilities. With respect to this latter disagreement, *Downs et al.*⁵ note that the proportion of the conformers is not well defined through the electron scattering, the estimated abundances of the rotamers carry a large uncertainty. The question is whether this wrong ratio had an effect on the other parameters obtained from the electron diffraction data. *Császár* and co-workers⁴ in their electron-diffraction study on Me₄Sb₂ applied two totally different fixed conformer ratios in the refinement procedure. Both gave similar results indicating that the determination of the conformer ratio is very uncertain, but the other parameters do not depend strongly on its value. Finally, about the vibrational study of *Durig* and *Casper*² we note that it has been performed in liquid, while our theoretical value refers to the gas phase. Moreover, *Durig* and *Casper*² assumed that the intensities of the Raman peaks were proportional to the abundances of the rotamers. This premise is clearly questionable since the polarizability and its derivatives should be different in the two rotamers. The calculation of the rotameric ratio from the PE experiment is based on the assumption that the photoionization cross sections do not differ significantly for the orbitals concerned. This assumption is not generally valid, but for orbitals of comparable energy and similar character it is reasonable and probably gives more reliable results than the other two experimental techniques.

Conclusions

In this work we have investigated the structure and photoelectron spectrum of tetramethyldiarsane by ab initio methods. Full potential energy curve along the C-As-As-C torsion was calculated at the Hartree-Fock level, and complete geometry optimization was performed at HF, MBPT(2), and CCSD levels of theory. Two different minima have been found giving the first theoretical proof for the existence of two conformers in the gas phase. Most of the calculated geometrical parameters are in good agreement with the data obtained from electron diffraction. The largest difference between the calculations and the experiment has been found for the C-As-As-C dihedral angle in the *gauche* conformer. Explanation is given why the theoretical value is considered to be more accurate.

The ionization energies (IEs) have been calculated from Koopmans' theorem and by EOMIP-CCSD methods. The calculated IEs do not support the original assignment of the PE spectrum of Me₄As₂ as given by *Cowley et al.*³ Therefore, a

new assignment has been proposed: we assign the lowest-energy band (I_1) to both the *anti* and *gauche* forms. The next, less intense I_2 band is assigned to the *gauche* conformer, while the third, intense band (I_3) is again assigned to the *anti* form. This means that there is a substantial splitting of the lone pair energy levels in both the *anti* and *gauche* forms.

In order to give a qualitative explanation, we have studied the *s* character of the lone pairs in the Me_4E_2 molecules with E being nitrogen, phosphorus, arsenic, and antimony. A clear correlation between the lone pair splitting and the *s* character has been found. Thus the increasing *s* character explains the increasing splitting. It also correlates well with the increasing pyramidalization of the Me_2E moieties which can be explained by the increasing steric demand of the *s* type orbitals.

Finally, the rotameric composition in the gas phase has been derived from the relative stability of the two conformers

calculated at several levels of theory, and it has been compared to the values obtained by experiment. The calculated ratio of about 22% *gauche* and 78% *anti* is in good agreement with the experimental value corresponding to our new assignment of the PES. The electron-diffraction⁵ and Raman² experiments gave significantly different results, and the former seems even to estimate incorrectly the relative stability of the two conformers.

Acknowledgment. We are very grateful to Prof. László Szepes for his very important help in the interpretation of our results. We acknowledge the financial support from the Hungarian Scientific Research Foundation (OTKA, Grant No. F019263 and T016202). We are also grateful to Avanti AG. for their gracious support. The calculations have been performed on an IBM SP/2 computer at our Department.

JA964339Q