ON THE CONFORMATION OF UNSATURATED ARSINES*

HARTMUT SCHMIDT, ARMIN SCHWEIG and HANS VERMEER

Fachbereich Physikalische Chemie, Universität Marburg, D-3550 Marburg (W. Germany) (Received 8 March 1976)

ABSTRACT

The ground state conformations of dimethylvinylarsine, dimethylphenylarsine, allyldimethylarsine, and benzyldimethylarsine are studied both theoretically and by UV photoelectron spectroscopy. Special emphasis is laid on an elucidation of the various forces, including AsC hyperconjugation, that determine the conformers of these unsaturated arsines.

INTRODUCTION

Below we present a theoretical and photoelectron (PE) spectroscopic analysis of the conformations of dimethylvinylarsine (1), dimethylphenylarsine (2), allyldimethylarsine (3), benzyldimethylarsine (4). To our knowledge, no other attempts to establish the conformations of unsaturated arsines have been reported.



CONFORMATIONAL PREDICTIONS AND DISCUSSION

All conformational calculations are based on the CNDO/2 method for third-row molecules [2]. The geometries of the respective π parts of 1-4 (standard bond lengths and angles are assumed) and of the CAsMe₂ grouping (trimethylarsine geometry [3] is taken) are kept fixed for all conformations. For the allylarsine (3) and benzylarsine (4) two locations of the lone pair on arsenic are admitted, either *cis* to the π fragment (i.e. the

^{*}See ref. 1

lone pair (n) -cis conformations 5 and 6 illustrated below) or trans to it



(i.e. the lone pair (n) -trans conformations 7 and 8). In Figs. 1—6 the relative conformational energy (represented as $-\infty$ or $-\infty$) is plotted against the dihedral angle α (i.e. the torsional angle around the =C—As bond in 1 and 2 and the =C—CH₂— bond in 3 and 4) for vinylarsine (1), phenylarsine (2), n -cis allylarsine (3), n -trans allylarsine (3), n -cis benzylarsine (4) and n -trans benzylarsine (4), respectively. In some cases, more simple model compounds such as the unsubstituted n -cis (Fig. 3) and n -trans (Fig. 4)



Fig. 1. Potential (i.e. relative conformational energy) for internal rotation in dimethylvinylarsine (1) vs. the CCAsC dihedral angle α at different stages of π conjugative coupling between the AsMe, and vinyl groupings. For details see text.



Fig. 2. Potential (i.e. relative conformational energy) for internal rotation in dimethylphenylarsine (2) vs. CCAsC dihedral angle α at different stages of π conjugative coupling between the AsMe₂ and phenyl groupings. For details see text.



Fig. 3. Potential (i.e. relative conformational energy) for internal rotation in n-cis allylarsine and n-cis allyldimethylarsine (3) vs. the CCCAs dihedral angle α at different stages of π -conjugative coupling between the CH₂AsH₂ or CH₂AsMe₂ and vinyl groupings. For details see text

allylarsine, as well as the unsubstituted *n*-trans benzylarsine (Fig. 6), are also considered. According to the results shown in these Figs. the most stable conformations of 1-4 are *n*-cis for 1 and 2 ($\alpha = 229$ and 49° ,



Fig. 4. Potential (i.e. relative conformational energy) for internal rotation in n-trans allylarsine and n-trans allyldimethylarsine (3) vs. the CCCAs dihedral angle α at different stages of π conjugative coupling between the CH₂AsH₂ or CH₂AsMe₁ and vinyl groupings. For details see text.

Fig. 5. Potential (i.e. relative conformational energy) for internal rotation in n - cis benzyldimethylarsine (4) vs. the CCCAs dihedral angle α at different stages of π conjugation coupling between the CH₁AsMe₁ and the phenyl groupings and at two selected C(Ph)CAs bond angles. For details see text.

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Fig. 6. Potential (i.e. relative conformational energy) for internal rotation in n-trans benzylarsine and n-trans benzyldimethylarsine (4) vs. the CCCAs dihedral angle α at different stages of π conjugative coupling between the CH₂AsH₂ or CH₂AsMe₂ and the phenyl groupings. For details see text.

respectively, meaning that the molecular plane bisects the MeAsMe angle), n-cis, As-cis ($\alpha = 0^{\circ}$) or n-trans, As-gauche ($\alpha = 90^{\circ}$) for 3 and n-cis, As-cis ($\alpha = 0^{\circ}$ when the =CCH₂As angle is a little widened, otherwise $\alpha = 20^{\circ}$) or n-trans, As-gauche ($\alpha = 90^{\circ}$) for 4.

Figures 1–6 contain some further results (curves represented as $-\Delta$ -- or ----- and -x - which allow some insight into the forces which determine the conformations given above. The dashed curves present the conformational energy relative to the most stable conformation, with all conjugative interactions between the π systems of the vinyl and phenyl parts and the substituents interrupted [4]. Hence these curves mainly reflect the steric conformational effects. The solid curves (-x-) display the same sort of relative conformational energy but this time with a selective interruption of the d_{π} -substituent/ π -system interactions [5]. Consequently, the energy difference between the latter curves (-x -) and the steric curves $(--\Delta -)$ or -----) reflect the effects of the remaining relative conjugative interactions (AsC and CH hyperconjugation and n/π conjugation) between the substituents and the π systems. Moreover, the relative $p_{\pi}d_{\pi}$ effects are equal to and the curves with $p_{\pi}d_{\pi}$ conjugative effects excluded (-x-). To demonstrate the use of the aforementioned partial contributions let us turn to Fig. 1 as a representative example. On first concentrating on the steric (------) and the total conformational energy (------) curves we immediately recognize that the most stable conformation of 1 is determined by conjugative and not by steric effects. We further see that the total relative conjugation energy (cf. the difference between both curves mentioned above) is less favorable for all other conformations than for the most stable one. This is equally true for both the individual $p_{\pi}d_{\pi}$ (cf. the difference between the ---- and --x - curves) and hyper-plus *n*-conjugative (cf. the difference between --x - and ----- curves) contributions.

Considering that the relative $p_{\pi}d_{\pi}$ and hyper-plus *n*-conjugative contributions may be opposite in sign (as e.g. in Fig. 2) all remaining cases shown in Figs. 2-6 can be similarly analyzed. Thus it follows that 2 in its most stable conformation is both favored by steric and hyper-plus *n*-conjugative effects but disfavored by $p_{\pi}d_{\pi}$ interferences (Fig. 2). The *n*-cis, As -cis form of 3 and the unsubstituted allylarsine (Fig. 3) is completely determined by steric interaction. The conjugative interferences (here mostly AsC hyperconjugation) would be most favorable in the gauche form. Turning first to the unsubstituted n -trans of 3 (Fig. 4) two stable forms of similar energy are predicted to occur: an As -*cis* ($\alpha = 0^{\circ}$) and an As -*gauche* $(\alpha = 90^{\circ})$ form. The first form occurs on steric and the second one on AsC hyperconjugative and $p_{\pi}d_{\pi}$ conjugative grounds. The As -*cis* form of *n*-trans 3 does not occur because of strong steric Me/ethylene inhibition and the realized As -gauche form constitutes a compromise between AsC hyperconjugative and $p_{\pi}d_{\pi}$ conjugative forces on the one hand and steric forces on the other. For n -cis 4 the As -cis form is realized although both the $p_{\pi}d_{\pi}$ and the AsC hyperconjugative interaction are most favorable in the As -gauche conformation (Fig. 5). Finally, the steric constraints for *n*-trans 4 are so severe that the molecule prefers an $\alpha = 90^{\circ}$ conformation despite the finding that for a little smaller or greater angles the conjugative effects are more favorable. In accordance therewith unsubstituted *n*-trans benzylarsine should exist in gauche conformations with $\alpha = 70$ and 110° (Fig. 6).

Since the *n*-trans, As -gauche and *n*-cis, As -cis forms of 3 as well as of 4 are expected to exhibit rather different UV photoelectron (PE) spectra because of AsC hyperconjugation present or not on symmetry reason—PE spectroscopy should be well suited to discriminate between the two alternatives. Therefore we undertake a PE study of 3 and 4 as well as of 1 and 2. The results are presented in the next section.

PHOTOELECTRON SPECTRA OF DIMETHYLVINYLARSINE (1), DIMETHYLPHENYL-ARSINE (2), ALLYLDIMETHYLARSINE (3), AND BENZYLDIMETHYLARSINE (4) AND DISCUSSION

Figures 7-10 show the low-energy parts of the photoelectron spectra of dimethylvinylarsine (1), dimethylphenylarsine (2), allyldimethylarsine (3), and benzyldimethylarsine (4). From a knowledge of the PE spectra of trimethylarsine [6], ethylene [7], and benzene [7] four ionization events ((1)-(4)) are expected to occur for 1 and 3 in the spectral regions shown and five events ((1)-(5)) for 2 and 4. These are the two AsC and the n

Fig. 7. Section of photoelectron spectrum of dimethylvinylarsine (1) with assignments. The numbers associated with each band are vertical ionization potentials in eV.

Fig. 8. Section of photoelectron spectrum of dimethylphenylarsine (2) with assignments. The numbers associated with each band are vertical ionization potentials in eV.

Fig. 9. Section of photoelectron spectrum of allyldimethylarsine (3) with assignments. The numbers associated with each band are vertical ionization potentials in eV.

Fig. 10. Section of photoelectron spectrum of benzyldimethylarsine (4) with assignments. The numbers associated with each band are vertical ionization potentials in eV. ionizations of the CAsMe₂ part and one or two π ionizations from the ethylene or benzene moieties, respectively. The ordering of these events follows from the comparison with the corresponding ionizations in the reference compounds and from the expected [8] influence of AsC hyperconjugation on the ionizations of the unsaturated arsines as documented in the correlation diagrams of Figs. 11-14.

Fig. 11. Correlation diagram for the lowest ion states of ethylene, dimethylvinylarsine (1), and trimethylarsine. The arrows represent the state shifts in the unsaturated arsine relative to corresponding states in ethylene and trimethylarsine. In text, it is assumed that the found shifts are due to localized orbital interactions.

Fig. 12. Correlation diagram for the lowest ion states of benzene, dimethylphenylarsine (2), and trimethylarsine.

Fig. 13. Correlation diagram for the lowest ion states of ethylene, allyldimethylarsine (3) and trimethylarsine. The black arrows represent the state shifts in the unsaturated arsine relative to corresponding states in ethylene and trimethylarsine thought to be due to AsC hyperconjugation. The white arrow represents the π state shift supposed to be caused by CH hyperconjugation.

Fig. 14. Correlation diagram for the lowest ion states of benzene, dimethylphenylarsine (2), benzyldimethylarsine (4), and trimethylarsine.

In agreement with the conformational predictions for 1 and 2 Figs. 11 and 12 indicate no n/π interaction in these molecules. Whilst Fig. 11 reflects strong AsC hyperconjugation this type of interaction cannot be read out from Fig. 12. The latter result can be simply understood. Assuming that the π/AsC ion states reflect pure localized orbital interactions [9] an interaction integral $H_{\pi\pi} = 0.61$ eV may be derived for 1 [10]. Taking the same value for 2 [11], the $\pi(b_1)$ ionization (Fig. 12) should occur at only about 0.2 eV lower energy than the $\pi(a_2)$ event which is not sufficient to resolve the corresponding PE bands.

From Fig. 13 it is obvious that 3 must exist in the *n*-trans, As -gauche form and not in the *n*-cis, As -cis form since only the gauche form can experience AsC hyperconjugation. Making the same assumption as in the preceding paragraph $H_{\pi\pi}$ amounts to 0.83 eV for AsC hyperconjugation alone [12]. The somewhat higher value in the allyl case may be due to either small d_{π}/π interaction in the vinyl case or better AsC/ π overlap in the allyl case or both mechanisms operating simultaneously [4].

The ionization correlation diagram of Fig. 14 is only in harmony with 4 existing in its *n*-cis, As -cis form. Given the *n*-trans, As -gauche form the missing splitting of the π states [13] which is expected here on the basis of the allyl H_{$\pi\pi$} value to be about 0.4 eV and the unusually low-lying *n* state, would remain unexplained. On the other hand, for the *n*-cis, As -cis form AsC hyperconjugation is excluded by symmetry and the low-lying *n*-state easily explained by *n*/CH(ring) interactions. The latter sort of interaction is evident from the CNDO/2 *n*-orbital contour plot [14-21] shown in Fig. 15.

In brief, the PE spectroscopic results are in accordance with the predicted conformations of 1-4. Particularly for 3 and 4, the method allows one to discriminate between two possibilities. Accordingly, allyldimethylarsine (3) exists in an As -gauche form, but benzyldimethylarsine in an As -cis form. The latter result is rather surprising.

EXPERIMENTAL SECTION*

Dimethylvinylarsine (1). A mixture of tetravinylstannane (8.28 g, 36.5 mmol) and dimethyliodoarsine [23] (8.46 g, 36.5 mmol) was heated at 150° for 6 h in a dry nitrogen atmosphere. The reaction mixture was fractionally distilled to give 1 (4.48 g, 93%), b.p. 65° (lit. [24] b.p. 79–80°). ¹H NMR (CD₂Cl₂) 6.59 (dd, 1H, ${}^{3}J_{cis} = 11.5$, ${}^{3}J_{trans} = 18.4$ Hz, vinylic H), 5.77 (dd, 1H, ${}^{2}J = 1.8$, ${}^{3}J_{cis} = 11.5$ Hz, vinylic *cis*-H), 5.57 (dd, 1H, ${}^{2}J = 1.8$, ${}^{3}J_{trans} = 18.4$ Hz, vinylic *trans*-H), 1.00 (s, 6 H, CH₃).

Anal. Calc. for C₄H₉As: C, 36.39; H, 6.87. Found: C, 36.52; H, 6.88. Treatment of the arsine 1 with methyl iodide in ether at room temperature under a nitrogen atmosphere quantitatively gave trimethylvinylarsonium iodide (1a), m.p. 270° after crystallization from ethyl acetate.

^{*}See ref. 22.

Fig. 15. Section of the electron density map of the *n* orbital of *n*-cis, As -cis benzyldimethylarsine (4) in the molecular plane. The deformation of the *n* orbital as a consequence of its interaction with a high-lying ring σ orbital (mainly of the CH type) is directly evident from the picture. In order to get a correct representation of orbital properties [20] the Löwdin transformed [15] CNDO/2 orbital was used to draw the density contours.

Anal. Calc. for C₅H₁₂AsI: C, 21.92; H, 4.41; I, 46.32. Found: C, 21.84; H, 4.29; I, 46.15.

Dimethylphenylarsine (2). This arsine was prepared by modification of the method of Burrows and Turner [25]. A solution of the Grignard compound, prepared from bromobenzene (7.9 g, 50.3 mmol) and magnesium (1.2 g, 50.0 mg-atom) in anhydrous ether (60 ml), was added dropwise to dimethyliodoarsine [23] (10.1 g, 43.6 mmol) in anhydrous ether (50 ml) under a dry nitrogen atmosphere. After the addition was complete, the reaction mixture was refluxed for 1 h, cooled, and hydrolyzed with degassed aqueous 10% NH₄Cl (20 ml). The organic layer was separated, washed with degassed water (15 ml) and dried over anhydrous Na₂SO₄. The ether was removed under reduced pressure, and the resulting liquid was fractionally distilled to give 2 (6.7 g, 84.5%), b.p. 78°/14 mm (lit. [25, 26] b.p. 85°/14 mm, 88–90°/18 mm). ¹H NMR (CDCl₃) 7.55–7.10 (m, 5H, aromatic H), 1.14 (s, 6H, CH₃).

Anal. Calc. for C₈H₁₁As: C, 52.77; H, 6.09. Found: C, 52.46; H, 5.89.

Allyldimethylarsine (3). Using the procedure described for the preparation of 2, 3 was obtained by the addition of allylmagnesium bromide, prepared from allyl bromide (15.32 g, 134 mmol) and magnesium (3.28 g, 135 mg-atom) in anhydrous ether (100 ml), to dimethyliodoarsine [23] (24.0 g, 103 mmol) in anhydrous ether (50 ml). Because of the extreme air-sensitivity of 3 the reaction was performed in a dry argon atmosphere. After hydrolysis with degassed aqueous 10% NH₄Cl (40 ml), work-up in the usual manner gave 3 (11.2 g, 74%), b.p. 103° (lit. [27] b.p. 108–110°). ¹H NMR (CDCl₃) 5.96–5.58 (m, 1 H, vinylic H), 5.05–4.79 (m, 2H, vinylic H). 2.22 (dd, 2H, ³ $J_{CH_2-vinylic H} = 7.8$, ⁴ $J_{CH_2-H_{cis}} = 1.3$, ⁴ $J_{CH_2-H_{trans}} = 0.8$ Hz, CH₂), 0.90 (s, 6H, CH₃).

Anal. Calc. for C₅H₁₁As: C, 41.12; H, 7.59. Found: C, 41.97; H, 7.11.

3 (1.0 g, 6.85 mmol) was methylated with methyl iodide (5 ml) in a manner identical with that employed in the preparation of <u>1a</u>. Recrystallization from ethyl acetate—methanol gave allyltrimethylarsonium iodide (1.9 g, 96%), m.p. 181–182° (lit. [27] 184–186°).

Anal. Calc. for C₆H₁₄AsI: C, 25.02; H, 4.90; I, 44.07. Found: C, 24.84; H, 4.68; I, 44.22.

Benzyldimethylarsine ($\frac{4}{2}$). Following the procedure described for the synthesis of 2, benzylmagnesium chloride, prepared from benzyl chloride (10.1 g, 80 mmol) and magnesium (1.95 g, 80 mg-atom) in anhydrous ether (60 ml), was added dropwise to dimethyliodoarsine [23] (13.9 g, 60 mmol) in anhydrous ether (50 ml) under a dry argon atmosphere. Reaction work-up gave $\frac{4}{2}$ (9.89 g, 84%), b.p. 106°/20 mm (lit. [28, 29] b.p. 110°/8 mm, 97–100°/9 mm). ¹H NMR (CDCl₃) 7.42–6.96 (m, 5H, aromatic H), 2.77 (s, 2H, CH₂), 0.88 (s, 3H, CH₃).

Anal. Calc. for $C_9H_{13}As: C$, 55.12; H, 6.68. Found: C, 55.00; H, 6.51. <u>4</u> (2.20 g, 11 mmol) was allowed to react with methyl iodide (5 ml) in anhydrous ether (20 ml) under an argon atmosphere. After work-up, the salt was recrystallized from ethanol to give benzyltrimethylarsonium iodide (3.70 g, 98%), m.p. 192° (lit. [28, 29] m.p. 195–196°, 202°).

Anal. Calc. for C₁₀H₁₆AsI: C, 35.53; H, 4.77; I, 37.54. Found: C, 35.28; H, 4.60; I, 37.43.

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- 13 It must be stressed that this type of splitting has been observed for all other benzyl compounds studied so far. See ref. 4.
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