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Molecular Structures of Methyldifluoroarsine, CH_3AsF_2, and Dimethylfluoroarsine, $(CH_3)_2AsF$, in the Gas Phase As Determined by Electron Diffraction and *ab Initio* Calculations[†]

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The structures of gaseous CH_3AsF_2 and $(CH_3)_2AsF$ have been determined by electron diffraction incorporating vibrational amplitudes derived from *ab initio* force fields scaled by experimental frequencies and, for the difluoride, restrained by microwave constants. The following parameters ($r_\alpha°$ structure, distances in pm, angles in degrees) have been determined for CH_3AsF_2: $r(\text{As}-\text{C}) = 194.6(4)$, $r(\text{As}-\text{F}) = 173.1(1)$, $\angle\text{CAsF} = 95.2(1)$, $\angle\text{FAsF} = 97.0(1)$. For $(CH_3)_2AsF$ structural refinement gives $r(\text{As}-\text{C}) = 195.1(1)$, $r(\text{As}-\text{F}) = 175.4(1)$, $\angle\text{CAsF} = 95.3(5)$, and $\angle\text{CAsC} = 96.9(8)$. For the series $(CH_3)_3As$, $(CH_3)_2AsF$, CH_3AsF_2, and AsF_3, both As−C and As−F bond lengths are shortened with increasing numbers of F atoms, but the angles CAsF and FAsF are almost invariant.

Introduction

Methyl derivatives of arsenic trifluoride have been known for some time; methyldifluoroarsine, CH_3AsF_2, was first synthesized by Emeléus et al. in 1946,[1] and the dimethyl derivative, $(CH_3)_2AsF$, by Bunsen as long ago as 1841.[2] Both compounds are viscous liquids at room temperature; the normal boiling points are reported to be 76.5 and 75 °C for CH_3AsF_2 and $(CH_3)_2AsF$, respectively.[1,3] Unlike the corresponding phosphines,[4] they are relatively robust, the neat liquids decomposing only slowly at 140 °C.

Here we report the results of an investigation into the structures of the gaseous molecules CH_3AsF_2 and $(CH_3)_2AsF$ based primarily on gas-phase electron-diffraction (GED) measurements. The structural refinement of the monomethyl derivative was expected to give problems of correlation associated with the similar F···F and F···C nonbonded distances. To overcome this problem, we have undertaken a combined analysis of the GED data and microwave rotation constants. In addition, *ab initio* calculations allied to vibrational analysis, as an independent means of calculating vibrational amplitudes and so constraining the models, have been used in both refinements. The success of this strategy has been demonstrated previously for the boron hydride molecules $HGa(BH_4)_2$[6] and $1\text{-}(Cl_2B)B_5H_8$.[7] The gaseous molecules AsF_3 and $(CH_3)_3As$ having already been characterized,[8−10] the structures of CH_3AsF_2 and $(CH_3)_2AsF$ are discussed in terms of the trends they reveal within the series of compounds $(CH_3)_{3-x}AsF_x$ (for $x = 0-3$).

Experimental Section

Synthesis. Samples of the methylfluoroarsines were prepared by metathetical fluorination of the corresponding iodoarsines, in line with procedures described in earlier reports.[1,2] Silver(I) fluoride was used as the fluorinating agent, the reactions being carried out in Teflon-FEP apparatus with poly(tetrafluoroethylene) couplings and needle valves (Production Techniques Ltd.). The reactions were performed at room temperature, although gentle warming of the sample of CH_3AsI_2 to temperatures above its melting point (30 °C)[11] was required to initiate exchange. Samples of methyldiiodoarsine and dimethyliodoarsine were prepared by established routes.[11] Silver(I) fluoride was used either as supplied (Aldrich) or as prepared by the action of aqueous HF (40%, BDH) on silver(I) carbonate.[12]

The compounds were purified by trap-to-trap distillation in vacuo, and their purity was assessed by ^{19}F NMR measurements made with CCl_3F solutions at 20 °C. CH_3AsF_2: ^{19}F NMR, $\delta_F = -113.0$, broad; ^1H NMR, $\delta_H = 1.84$, triplet; $^3J(F,H) = 14.8$ Hz. $(CH_3)_2AsF$: ^{19}F NMR, $\delta_F = -225.0$, septet; ^1H NMR, $\delta_H = 1.76$, doublet; $^3J(F,H) = 13.3$ Hz.

The sample of CD_3AsF_2 was produced by fluorination of the corresponding iodide, the preparation of which employed CD_3I to introduce the labeled methyl constituent.[11] Iodomethane-d_3 was in turn

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[†] This paper is dedicated by A.J.D. to Professor Dr. mult. Alois Haas of the Ruhr-Universität Bochum to mark his 65th birthday.

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Table 1. Nozzle-to-Plate Distances, Weighting Functions, Correlation Parameters, Scale Factors, and Electron Wavelengths Used in the Electron-Diffraction Study

compound	nozzle-to-plate distance/mm	weighting functions/nm^{-1}					correln param	scale factor/k^{a}	electron wavelength^{b}/pm
		Δs	s_{min}	sw_1	sw_2	s_{max}			
CH_3AsF_2	285.90	2	20	40	122	144	0.417	0.964(16)	5.676
	128.20	4	60	80	260	300	0.053	0.773(16)	5.676
$(CH_3)_2AsF$	285.90	2	20	40	122	144	0.341	1.021(17)	5.676
	128.20	4	60	80	260	300	−0.185	0.937(17)	5.676

[a] Figures in parentheses are the estimated standard deviations. [b] Determined by reference to the scattering pattern of benzene vapor.

prepared by the reaction of anhydrous methanol-d_4 (Aldrich) with red phosphorus (Aldrich) and crystalline iodine (Aldrich).[13]

Electron-Diffraction Measurements. Electron-scattering intensities were recorded on Kodak Electron Image plates using the Edinburgh gas-diffraction apparatus operating at *ca.* 44.5 kV (electron wavelength *ca.* 5.7 pm).[14] Measurements were made using a stainless steel inlet system and aluminum nozzle; the sample and nozzle temperatures were *ca.* 293 K during the exposure periods. Nozzle-to-plate distances were *ca.* 128 and 286 mm, yielding data in the s range 20−300 nm^{-1}; for each compound two plates at each camera distance were selected for analysis. The scattering patterns of benzene were also recorded for the purpose of calibration.

Nozzle-to-plate distances, weighting functions used to set up the off-diagonal weight matrices, correlation parameters, final scale factors, and electron wavelengths for the measurements are collected together in Table 1.

The electron-scattering patterns were converted into digital form using a computer-controlled Joyce-Loebl MDM6 microdensitometer with a scanning program described elsewhere.[15] The programs used for data reduction[15] and least-squares refinement[16] have been described previously; the complex scattering factors employed were those listed by Ross *et al.*[17]

Theoretical Calculations. All calculations were performed on Dec Alpha 1000 4/200 workstations using the Gaussian 94 program.[18] Geometries were optimized using analytic first derivatives while vibrational frequencies were calculated from analytic second derivatives. Preliminary calculations on CH_3AsF_2 and $(CH_3)_2AsF$ (both with C_s symmetry) were performed at the SCF and MP2 levels of theory using the 6-31G** basis sets.[19−21] We wished to investigate the effects of both diffuse functions and a more complete correlation treatment on the molecular geometry, and so additional calculations were performed at the MP2/6-31+G** and MP4SDQ/6-31G** levels for CH_3AsF_2. Final geometries were obtained using a basis set of TZ2P(f) quality. The larger arsenic basis was constructed from the [15s, 12p, 9d] primitive set of Sadlej,[22] supplemented with a single set of f-type functions (exponent 0.40) and contracted to (11s, 9p, 5d, 1f). No additional d-type functions were added to this basis set since the three outermost d-type functions (exponents 0.328 25, 0.103 36, and 0.032 547) are sufficiently diffuse to polarize the 4d electrons. The arsenic basis set was then combined with basis sets of comparable size[23] for fluorine and carbon {both [10s, 6p, 2d]/(5s, 3p, 2d)} and hydrogen {[5s, 2p]/(3s, 2p)} to form the TZ2P(f) basis (polarization exponents were 3.50 and 0.85 for fluorine, 1.20 and 0.30 for carbon, and 1.50 and 0.40 for hydrogen). Geometry optimizations were performed at the SCF and MP2 levels of theory using the TZ2P(f) basis set for both molecules, while a further calculation in which all the electrons were included in the correlation treatment, MP2(FULL), was undertaken for CH_3AsF_2 to investigate the effects of core correlation.

Vibrational frequency calculations were performed at the MP2/6-31G** level for CH_3AsF_2 and $(CH_3)_2AsF$ to verify that both structures represent local minima on the potential-energy surface and to calculate the vibrational amplitudes needed to assist in the refinement of the electron-diffraction data. The Cartesian force field was converted to one described by symmetry coordinates using the program ASYM40.[24]

Vibrational Spectroscopic Measurements. IR spectra were recorded in the range 4000−400 cm^{-1} using Perkin-Elmer 1710 and Mattson Galaxy FT-IR instruments. Raman spectra were excited at $\lambda = 514.5$ nm with the output of a Spectra-Physics Model 165 Ar^+ laser and measured with a Spex Ramalog 5 spectrophotometer. Solid films of the volatile materials were presented for spectroscopic analysis by condensing the vapor on a CsI window (for IR measurements) or a copper block (for Raman measurements) contained in an evacuated shroud and maintained at 77 K. The spectra of the vapors were recorded using a stainless steel infrared cell fitted with silver chloride windows.

Molecular Models

CH_3AsF_2. The positions of the heavy atoms were defined by two distances and two angle parameters: the As−C distance, p_1; the As−F distance, p_4; the average of the heavy atom angles, $[2(\angle CAsF) + (\angle FAsF)]/3$, p_5; and the difference of the angles, $[(\angle FAsF) - (\angle CAsF)]$, p_6. The CH_3 group was assumed to have local C_{3v} symmetry and to be staggered with respect to the AsF_2 unit in the starting conformation, *i.e.* giving the molecule overall C_s symmetry. It was then defined by four parameters: the C−H distance, p_2; the angle between the C−H bonds and the C_3 axis, p_3; the tilt of the CH_3 unit in the As(1)C(4)H(5) plane, p_8, defined as positive for As−C−H(5) decreasing; and a parameter defining the nature of the rotation of the methyl group about its local C_3 axis, p_7. In the initial refinements, this parameter was defined as a twist angle about the local C_3 axis, allowing the overall symmetry to fall to C_1 except when $p_7 = 0°$ (C_s staggered) or 180° (C_s eclipsed). In the later refinements, however, this parameter was defined as a potential energy barrier to free rotation (V_0) of the CH_3 group about its local C_3 axis. This was achieved by representing the rotation as a set of fixed conformations of the CH_3 group over the range $0° \leq \phi \leq 60°$ of the rotation angle, ϕ ($\phi = 0°$ defined as the C_s staggered conformation). Thus, the continuous torsion-sensitive distance distribution was approximated by calculating the nonbonded distances $r(F\cdots H)$ and $r(As\cdots H)$ at angle increments $\Delta\phi = 10°$; 54 distinct torsion-sensitive distances were generated by this scheme. The low-barrier classical

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Table 2. Observed and Calculated Vibrational Frequencies (cm^{-1}) for CH_3AsF_2

irred rep	mode	CH_3AsF_2 obs[a]	CH_3AsF_2 calc[b]	CD_3AsF_2 obs[a]	CD_3AsF_2 calc[b]	approx descripn of mode
a′	ν_1	3014	3029	2261	2246	ν_{asym}(C−H)
	ν_2	2924	2948	2130	2113	ν_{sym}(C−H)
	ν_3	1418	1421	1031	1025	$\delta_{asym}(CH_3)$
	ν_4	1256	1253	981	984	$\delta_{sym}(CH_3)$
	ν_5	816	814	690	695	$\rho(CH_3)$
	ν_6	697	692	*c*	640	ν_{sym}(As−F)
	ν_7	595	597	540	538	ν(As−C)
	ν_8	296[d]	304	287[e]	292	AsF_2 wag[f]
	ν_9	255[d]	254	245[e]	240	$\delta(AsF_2)$[f]
a″	ν_{10}	2995	3016	2247	2235	ν_{asym}(C−H)
	ν_{11}	1412	1420	1028	1026	$\delta_{asym}(CH_3)$
	ν_{12}	805	805	665	671	$\rho(CH_3)$
	ν_{13}	673	667	625	625	ν_{asym}(As−F)
	ν_{14}	240[d]	241	220[e]	209	AsF_2 rock
	ν_{15}	*g*	208	*g*	157	CH_3 torsion

[a] Except where stated, frequencies are taken from the infrared spectrum of the vapor. [b] From the scaled theoretical force field. [c] Obscured by CD_3 rocking fundamentals. [d] Values taken from the Raman spectrum of a pure liquid sample. [e] Values taken from infrared spectrum of the solid. [f] ν_8 and ν_9 are strongly coupled together. [g] Not observed.

approximation for the probability distribution of the rotation angle (ϕ)

$$P(\phi) = N[\exp(-V(\phi)/RT)]$$

was adopted, and the potential function was assumed to be of the form

$$V(\phi) = V_0/2[1 - \cos(3\phi)]$$

as indicated by the theoretical study (see below). The relative multiplicities of the 36 r(F···H) and 18 r(As···H) distinct nonbonded distances were weighted according to P(ϕ).

$(CH_3)_2AsF$. The heavy-atom positions were again defined by two distance and two angle parameters: the As−F distance, p_1; the As−C distance, p_2; the CAsF angle, p_4; and the CAsC angle, p_5. The positions of the hydrogen atoms were defined by the C−H distance, p_3, the AsCH angle, p_6, and the methyl twist, p_7. The twist angle is such that it rotates the two methyl groups while preserving C_s symmetry, clockwise about C(6)−As(10) and anticlockwise about C(2)−As(10), from the initial position with F(1)As(10)C(2)H(5) = 0°.

Results

Refinement of the Structures. The gas-phase structures of CH_3AsF_2 and $(CH_3)_2AsF$ were refined in r_α° space. Harmonic vibrational force fields were computed for both molecules at the MP2/6-31G** level of theory and the program ASYM40[24] was used to convert the Cartesian force fields to those described by symmetry coordinates; the internal coordinates used are given in the Supporting Information. An optimum fit of the theoretical to the experimental vibrational frequencies (see Tables 2 and 3) was achieved in each case by a refinement of the *ab initio* force constants using a set of scaling factors, 10 for CH_3AsF_2 and 7 for $(CH_3)_2AsF$. Root-mean-square amplitudes of vibration (u) and perpendicular amplitudes of vibration (K) were then calculated from the scaled force constants using ASYM40.

The microwave (MW) spectrum of CH_3AsF_2 has been analyzed by Nugent and Cornwell[25] to yield three ground-state rotation constants (B_0). These were converted to B_z values using harmonic vibrational corrections derived from the theoretical force field, and a combined analysis of the GED data and MW constants was undertaken for CH_3AsF_2.

Table 3. Observed and Calculated Vibrational Frequencies (cm^{-1}) for $(CH_3)_2AsF$

irred rep	mode	$(CH_3)_2AsF$ obs[a]	$(CH_3)_2AsF$ calc[b]	approx descripn of mode
a′	ν_1	2998	3016	ν_{asym}(C−H)
	ν_2	2998	3003	ν_{asym}(C−H)
	ν_3	2920	2898	ν_{sym}(C−H)
	ν_4	1432	1440	$\delta_{asym}(CH_3)$
	ν_5	1419	1421	$\delta_{asym}(CH_3)$
	ν_6	1260	1266	$\delta_{sym}(CH_3)$
	ν_7	893	894	$\rho(CH_3)$
	ν_8	818	813	$\rho(CH_3)$
	ν_9	640	640	ν(As−F)
	ν_{10}	590	587	ν_{sym}(As−C)
	ν_{11}	269[c]	279	AsC_2 wag[d]
	ν_{12}	233[c]	232	$\delta(AsC_2)$[d]
	ν_{13}	*e*	174	CH_3 torsion
a″	ν_{14}	2998	3015	ν_{asym}(C−H)
	ν_{15}	2998	3002	ν_{asym}(C−H)
	ν_{16}	2920	2899	ν_{sym}(C−H)
	ν_{17}	1419	1421	$\delta_{asym}(CH_3)$
	ν_{18}	1419	1410	$\delta_{asym}(CH_3)$
	ν_{19}	1244[c]	1250	$\delta_{sym}(CH_3)$
	ν_{20}	792[c]	787	$\rho(CH_3)$[f]
	ν_{21}	775	759	$\rho(CH_3)$[f]
	ν_{22}	590	593	ν_{asym}(As−F)
	ν_{23}	233	226	AsC_2 rock
	ν_{24}	*e*	127	CH_3 torsion

[a] Except where stated, frequencies are taken from the infrared spectrum of the vapor. [b] From the scaled theoretical force field. [c] Values taken from the Raman spectrum of the solid. [d] ν_{11} and ν_{12} are strongly coupled together. [e] Not observed. [f] ν_{20} and ν_{21} are strongly coupled together.

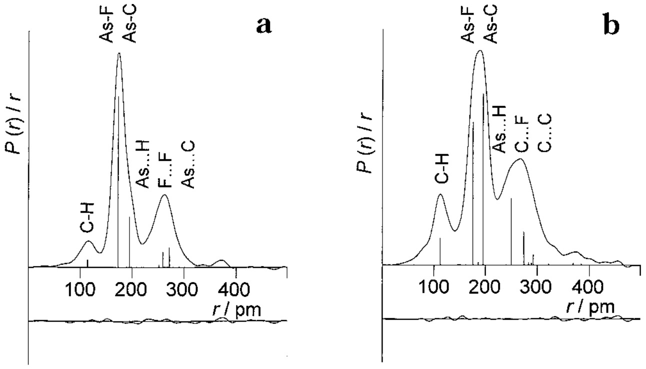

Figure 1. Observed and final weighted difference radial-distribution curves for (a) CH_3AsF_2 and (b) $(CH_3)_2AsF$. Before Fourier inversion the data were multiplied by $s\ \exp[(-0.00002s^2)/(Z_{As} - f_{As})(Z_F - f_F)]$.

CH_3AsF_2. The radial-distribution curve for CH_3AsF_2 (Figure 1a) consists of four distinct peaks centered at *ca.* 115, 173, 260, and 367 pm. The first two of these correspond to the bonding distances, the C−H pairs giving rise to the peak at 115 pm and the As−F and As−C pairs combining to give the intense peak at 173 pm. Scattering from the nonbonded, heavy-atom pairs As···F, F···F, and C···F accounts for the feature at 260 pm, while the peak at 367 pm is attributable to F···H scattering.

Starting from the geometry computed *ab initio* at the MP4SDQ/6-31G** level, and assuming C_s symmetry (*i.e.* fixing p_7 at 0°), refinement of the GED data combined with the three rotation constants proceeded straightforwardly. Of the other seven parameters defining the geometrical structure, all could be refined simultaneously except p_8, the methyl tilt angle. This

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would not refine freely and attempts were made subsequently to optimise it using a flexible restraint.[26,27]

Flexible parameter restraints may allow the refinement of parameters which would usually have to be fixed. Estimates of the values of these parameters and their uncertainties are used as additional observations in a combined analysis similar to those routinely carried out for electron-diffraction data combined with rotation constants and/or dipolar coupling constants. The starting values and uncertainties for the extra observations are derived from another method, such as X-ray diffraction or theoretical computations. *All* parameters are then included in the refinements. If the intensity pattern contains useful information concerning one of these parameters, the parameter in question will refine with an esd less than the uncertainty in the corresponding additional observation. However, if there is little or no relevant information, the parameter will refine with an esd equal to the uncertainty of the extra observation. In this case, the parameter can simply be fixed in the knowledge that doing this does not influence either the magnitudes or the esd's of other parameters. In some cases, because increasing the number of refining parameters allows all the effects of correlation to be considered, some esd's may actually increase. Overall, this approach utilizes all available data as fully as possible and returns more realistic esd's for the refined parameters.

Using a flexible parameter restraint of 0 ± 1°, it proved possible to refine p_8. Additionally, most of the amplitudes of vibration could be refined, either freely or tied in groups; ratios between amplitudes in these groups were taken from the theoretical force field. Amplitudes for the nonbonded As···H and F···H distances were refined subject to restraints of 12.4 ± 2.0 and 20.5 ± 4.0 pm, respectively.

In the later refinements, the constraint of C_s symmetry was lifted by allowing p_7, the methyl torsion parameter, to refine. As a result, the R_G value dropped from 0.074 to 0.073, yielding a structure having C_1 symmetry with $p_7 = 20(6)°$, *i.e.* r[F(2)···H(5)] = 259(4) and r[F(3)···H(5)] = 294(7) pm. It seems reasonable to think that this value for p_7 results from vibrational averaging of a large-amplitude torsional motion of the CH_3 group. Although this mode has not been located in the measured vibrational spectra, it is computed at the MP2/6-31G** level (scaled) to lie at 208 cm^{-1} (see Table 2), a low frequency for such a mode. To investigate this further, relative energies were calculated for conformations with the methyl torsion parameter (ϕ) fixed at values in the range $0° \leq \phi \leq 60°$ at 10° intervals while optimizing all other parameters at the MP2/6-31G** level. The variation of relative energy with ϕ is shown in Figure 2. It is found to be of the form $V(\phi) = V_0/2[1 - \cos(3\phi)]$ with a 3-fold barrier to rotation, V_0, of 5.85 kJ mol^{-1}. Since $RT = 2.4$ kJ mol^{-1} at 293 K, this is consistent with a large-amplitude torsional motion of the CH_3 group. Thus, in the final refinements, p_7 was redefined as the potential-energy barrier as described above.

$(CH_3)_2AsF$. The radial-distribution curve for $(CH_3)_2AsF$ (Figure 1b) shows two peaks in the region associated with bonded distances, with one at *ca.* 110 pm for the C−H distance and the other at *ca.* 185 pm for both the As−F and As−C distances. The very broad feature at *ca.* 265 pm is attributable mainly to scattering from the nonbonded As···H, C···F, and C···C pairs, with the least intense feature at *ca.* 373 pm corresponding to F···H and C···H nonbonded pairs.

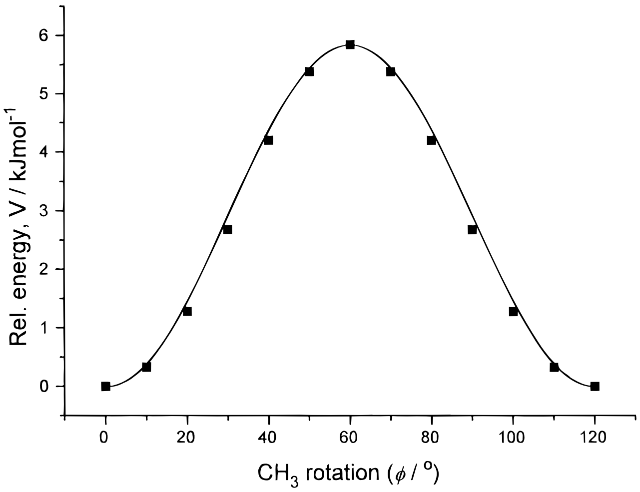

Figure 2. Variations of the theoretical relative energy, V/kJ mol^{-1}, with the methyl group rotation angle, ϕ/deg, for CH_3AsF_2. Points marked ■ were calculated for optimized geometries at the MP2/6-31G** level; the solid curve represents the function $V(\phi) = V_0/2\,[1 - \cos(3\phi)]$ for $V_0 = 5.85$ kJ mol^{-1}.

Table 4[a]

(a) GED Structural Parameters ($r_\alpha°$/pm, ∠α/deg, V_0/kJ mol^{-1}) for CH_3AsF_2[b]

	parameter	magnitude
p_1	As−C	194.6(4)
p_2	C−H	111.4(10)
p_3	C_3 axis−CH angle	106.5(17)
p_4	As−F	173.1(1)
p_5	av angle, [2(∠CAsF) + ∠FAsF]/3	95.81(3)
p_6	diff angle, ∠FAsF − ∠CAsF	1.8(2)
p_7	V_0	5.85(f)
p_8	CH_3 tilt	0.2(10)

(b) Interatomic Distances (r_a/pm) and Amplitudes of Vibration (u/pm) for CH_3AsF_2[c]

			amplitude	
	atom pair	dist	expt	calc[d]
r_1	As(1)−F(2)	173.2(1)	5.4(2)	4.2
r_2	As(1)−C(4)	194.7(4)	6.0(4)	5.2
r_3	C(4)−H(5)	114.8(10)	7.5(11)	7.8
r_4	F(2)···F(3)	259.0(1)	10.2(12)	8.6
r_5	F(2)···C(4)	271.6(5)	11.7(9)	9.4
r_6	As(1)···H(5)	251.0(23)	11.0(13)	12.4
r_7	As(1)···H(6)	251.5(21)	11.0 (tied to u_6)	12.4
r_8	As(1)···H(7)	251.4(20)	11.0 (tied to u_6)	12.4

(c) Microwave Rotation Constants (B/MHz) for CH_3AsF_2

axis	obs B_0	corr B_z	calc B_z	B_z diff (obs − calc)	uncertainty[e]	weight[f]
A	5414.49(15)	5406.69	5406.74	−0.05	0.79	0.2
B	5381.28(15)	5375.13	5375.16	−0.03	0.64	0.3
C	3871.88(15)	3869.29	3869.30	−0.01	0.30	1.4

[a] For atom-numbering scheme, see Figure 4a. Figures in parentheses are the estimated standard deviations. [b] For definitions of parameters see text; f = fixed. [c] H···H, H···F, and H···C nonbonded distances were also included in the refinements but are not listed here. [d] Amplitudes calculated at the MP2/6-31G** level. [e] Uncertainty = [(uncertainty in microwave measurement)^2 + 0.1(vibrational correction)^2]$^{1/2}$. [f] Relative to the GED data.

Initial refinements of the structure explored the conformational properties of the methyl hydrogen atoms, allowing rotations of the methyl groups about the As−C axes in identical or opposite directions from a series of different starting positions. Such refinements indicated an R_G minimum corresponding to overall C_s symmetry, and this was assumed subsequently.

It was possible to refine simultaneously all seven of the parameters defining the geometrical structure and all of the

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Table 5[a]

(a) GED Structural Parameters (r_α°/pm, ∠α/deg) for $(CH_3)_2AsF$[b]

	param	magnitude		param	magnitude
p_1	As−F	175.4(1)	p_5	∠CAsC	96.9(8)
p_2	As−C	195.1(1)	p_6	∠AsCH	106.7(7)
p_3	C−H	106.1(3)	p_7	CH_3 twist	57(11)
p_4	∠CAsF	95.3(5)			

(b) Interatomic Distances (r_a/pm) and Amplitudes of Vibration (u/pm) for $(CH_3)_2AsF$[c]

	atom pair	distance	amplitude (expt)	amplitude (calc)[d]
r_1	As(10)−F(1)	175.6(1)	5.7(2)	4.4
r_2	As(10)−C(2)	195.3(1)	6.2(2)	5.2
r_3	C(2)−H(3)	112.3(3)	6.6(4)	7.8
r_4	F(1)···C(2)	274.1(10)	9.2(10)	9.7
r_5	C(2)···C(6)	292.0(18)	7.5(23)	9.6
r_6	As(10)···H(3)	249.7(9)	11.3(7)	12.3

[a] For atom-numbering scheme, see Figure 4b. Figures in parentheses are the estimated standard deviations. [b] For definitions of parameters and flexible restraints used in the refinements see text. [c] H···H, H···F, and H···C nonbonded distances were also included in the refinements but are not listed here. [d] Amplitudes calculated at the MP2/6-31G** level.

Table 6. Least-Squares Correlation Matrices (×100)[a]

(a) CH_3AsF_2

p_3	p_4	p_5	p_6	u_1	u_4	u_5	u_6	k_1	k_2	
−91	53	57	−67	50	−56	−53		74	62	p_1
		70								p_2
	−67	−83	90	−52	60	56		−73	−63	p_3
		51	−79		−53	−50				p_4
			−90					56	50	p_5
					57	52		−58	−50	p_6
								66	79	u_1
							−52			u_4
									69	k_1

(b) $(CH_3)_2AsF$

p_6	p_7	u_2	u_5	u_6	u_{10}	k_1	k_2	
71	63				52			p_4
	64							p_5
					51	-54		p_6
		78				58	64	u_1
						58	64	u_2
			75	61				u_4
							66	k_1

[a] Only elements with absolute values ≥50% are shown; k is a scale factor.

vibrational amplitudes (u) except those for the H···H distances. One amplitude, u[C(2)···H(8)], was refined subject to a flexible restraint of 26.9 ± 5.0 pm.

The geometrical parameters and the most important dependent distances derived in the final refinements for CH_3AsF_2 and $(CH_3)_2AsF$ are listed in Tables 4 and 5; $R_G = 0.073$ ($R_D = 0.049$) for CH_3AsF_2 and $R_G = 0.071$ ($R_D = 0.057$) for $(CH_3)_2AsF$. Tables 4 and 5 also contain the calculated amplitudes of vibration for the purposes of comparison with those derived from the GED experimental data. The most significant elements of the least-squares correlation matrices are shown in Table 6, and Figure 3 illustrates the observed and final difference curves for the molecular-scattering intensities. The optimized experimental structures of the two molecules are shown in Figure 4.

***Ab Initio* Calculations.** Calculations with CH_3AsF_2 were performed at seven different levels in order to determine the effects of improving the theoretical treatment on the molecular geometry. Geometrical parameters are reported in Table 7. As

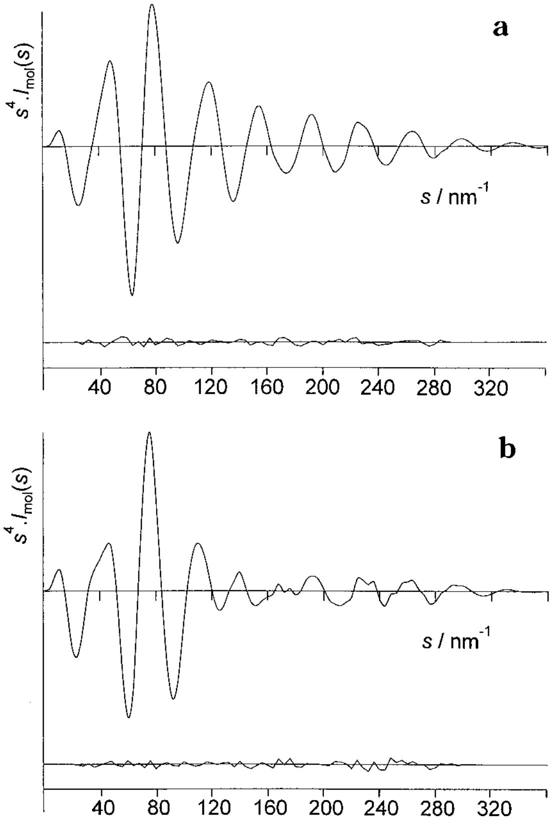

Figure 3. Observed and final weighted difference combined molecular-scattering intensity curves for (a) CH_3AsF_2 and (b) $(CH_3)_2AsF$. Theoretical data are shown for the regions 0−20 and 300−360 nm^{-1}, for which no experimental data are available.

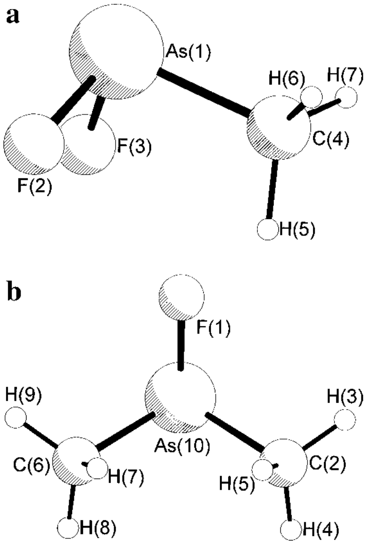

Figure 4. Views of (a) CH_3AsF_2 and (b) $(CH_3)_2AsF$ corresponding to parameters obtained in the optimum refinements.

might be expected,[28] estimates of bond lengths were generally predicted to be shorter at the SCF level as compared with correlated calculations. The introduction of electron correlation into the calculation was found to have a particularly large effect on the As−F bond, which increases in length from 171.2 pm (SCF/6-31G**) to 174.2 pm (MP2/6-31G**). However, improvements in the correlation treatment (to MP4SDQ) did not lead to further changes in the value of this parameter. The As−C bond, which was found to lengthen by 0.5 pm to 192.7

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Table 7. Theoretical Molecular Geometries (r_e/pm, ∠/deg) and Absolute Energies (hartrees) for CH_3AsF_2[a]

	6-31G**			6-31+G**	TZ2P(f)			
	SCF	MP2	MP4SDQ	MP2	SCF	MP2	MP2(FULL)	GED[b]
r(As−C)	192.2	192.7	193.4	192.3	193.3	193.4	193.4	194.6(4)
r(As−F)	171.2	174.2	174.2	175.6	171.0	174.5	174.6	173.1(1)
r[C−H(5)]	108.2	108.7	108.8	108.8	108.0	108.6	108.5	111.4(10)
r[C−H(6/7)]	108.4	108.9	108.9	108.9	108.2	108.8	108.7	111.4(10)
∠CAsF	95.8	95.3	95.1	95.1	96.1	95.4	95.4	95.2(1)
∠FAsF	95.8	97.0	96.7	96.7	95.7	96.7	96.6	97.0(1)
∠AsCH(5)	108.9	108.1	108.1	108.7	109.5	108.5	108.5	106.3(19)[c]
∠AsCH(6/7)	109.4	109.4	109.5	109.3	109.2	108.9	108.9	106.7(18),[c] 106.6(17)[c]
energy	−2470.531 960	−2471.128 735	−2471.155 726	−2471.186 580	−2472.796 806	−2473.724 335	−2474.104 848	

[a] For atom-numbering scheme, see Figure 4a. [b] $r_\alpha°$ structure. [c] Values for $\phi = 5°$.

Table 8. Molecular Geometries (r_e/pm, ∠/deg) and Absolute Energies (hartrees) for $(CH_3)_2AsF$[a]

	6-31G**		TZ2P(f)		
	SCF	MP2	SCF	MP2	GED[b]
r(As−F)	173.8	176.5	173.8	177.1	175.4(1)
r(As−C)	194.0	194.4	194.9	194.8	195.1(1)
r[C−H(3)]	108.3	108.7	108.1	108.6	106.1(3)
r[C−H(4)]	108.5	108.9	108.4	108.9	106.1(3)
r[C−H(5)]	108.3	108.8	108.1	108.7	106.1(3)
∠FAsC	96.0	95.9	96.3	96.0	95.3(5)
∠CAsC	98.4	97.0	98.6	96.2	96.9(8)
∠AsCH(3)	109.4	109.5	109.4	109.6	106.7(7)
∠AsCH(4)	109.0	108.8	108.9	108.3	106.7(7)
∠AsCH(5)	110.5	109.9	110.8	109.8	106.7(7)
energy	−2410.688 776	−2411.263 167	−2412.916 296	−2413.786 266	

[a] For atom-numbering scheme, see Figure 4b. [b] $r_\alpha°$ structure.

pm when the adopted level of theory was improved from SCF to MP2, lengthens further to 193.4 pm at the MP4SDQ/6-31G** level. Electron correlation was also found to be of some importance in describing the FAsC and FAsF bond angles, which are indistinguishable at the SCF level (both 95.8° at SCF/6-31G**) but differ by 1.7° at the MP2/6-31G** level (∠CAsF = 95.3° and ∠FAsF = 97.0°). The addition of diffuse functions (6-31+G** basis) was found to have little effect on molecular parameters except for the As−F bond, which is elongated by 1.4 pm at the MP2 level (6-31G** *vs* 6-31+G**).

Improving the basis set to TZ2P(f) proved to have only a minor effect on most molecular parameters although, significantly, the As−C bond distance once again becomes longer. Since improvements in both basis set and the treatment of electron correlation lead to the prediction of a longer As−C bond, it is probable that even more sophisticated calculations would predict further attenuation of the bond. A single geometry optimization performed at the MP2(FULL)/TZ2P(f) level showed that the effects of correlating core electrons are small.

Calculations with $(CH_3)_2AsF$ were performed at four different levels of theory, with the results presented in Table 8. Most molecular parameters, except the As−F bond length and CAsC angle, proved to be fairly insensitive to changes in either the basis set or the treatment of electron correlation. The As−F bond distance, as found for the difluoro compound, lengthens substantially when the effects of electron correlation are taken into account. The CAsC angle becomes narrower as the quality of the calculation is improved.

The Cartesian coordinates for both the theoretical and GED structures are given in Table 9.

Discussion

The structures deduced for the methylfluoroarsine derivatives CH_3AsF_2 and $(CH_3)_2AsF$ are in accord with those found for closely related molecules; in neither case do the methyl groups show properties out of the ordinary. The structural parameters determined experimentally for all the molecules in the series $(CH_3)_3As$, $(CH_3)_2AsF$, CH_3AsF_2, AsF_3 are gathered in Table 10.

Table 9. Atomic Coordinates (pm)

(a) CH_3AsF_2

	GED refinement ($r_\alpha°$)			*ab initio* [MP4SDQ/6-31G**] optimizn (r_e)		
atom	x	y	z	x	y	z
As(1)	0.0	0.0	0.0	0.0	0.0	0.0
F(2)	−156.3	−113.6	129.7	192.7	0.0	0.0
F(3)	−156.3	−113.6	−129.7	−16.0	−114.3	−130.5
C(4)	194.5	0.0	0.0	−16.0	−114.3	130.5
H(5)	226.5	−99.7	37.2	226.6	−103.3	0.0
H(6)	227.4	81.8	67.6	228.9	51.4	88.9
H(7)	227.0	17.4	−104.8	228.9	51.4	−88.9

(b) $(CH_3)_2AsF$

	GED refinement ($r_\alpha°$)			*ab initio* [MP2/TZ2P(f)] optimizn (r_e)		
atom	x	y	z	x	y	z
F(1)	0.0	0.0	0.0	0.0	0.0	0.0
C(2)	193.6	128.2	−146.0	197.4	128.5	−145.0
H(3)	151.0	82.8	−231.9	172.7	81.0	−239.5
H(4)	297.4	146.4	−157.9	301.4	160.9	−147.8
H(5)	140.8	215.4	−116.8	132.4	213.9	−127.9
C(6)	193.6	128.2	146.0	197.4	128.5	145.0
H(7)	140.8	215.4	116.8	132.4	213.9	127.9
H(8)	297.4	146.4	157.9	301.4	160.9	147.8
H(9)	151.0	82.8	231.9	172.7	81.0	239.5
As(10)	175.4	0.0	0.0	177.1	0.0	0.0

The As−F bond lengths for the series $(CH_3)_{3-x}AsF_x$ decrease systematically with increasing x, by 2.4 pm from $(CH_3)_2AsF$ to CH_3AsF_2 and by 2.8 pm from CH_3AsF_2 to AsF_3. The trend toward shorter As−F distances attending the substitution of fluorine for less electronegative methyl substituents is to be expected on the basis of decreased polarity or of reduced electron pair repulsion in the valence shell.

Table 10. Comparison of the Structural Parameters for Gaseous Molecules

(a) $(CH_3)_3As$, $(CH_3)_2AsF$, CH_3AsF_2, AsF_3[a,b]

param	$(CH_3)_3As$[10]	$(CH_3)_2AsF$[c]	CH_3AsF_2[c]	AsF_3[9]
r(As−C)	197.0(3)	195.5(1)	194.9(4)	
r(As−F)		175.8(1)	173.4(1)	170.6(2)
∠CAsC	96.1(5)	96.9(8)		
∠CAsF		95.3(5)	95.2(1)	
∠FAsF			97.0(1)	96.2(2)

(b) $(CH_3)_3P$, CH_3PF_2, PF_3[a,b]

param	$(CH_3)_3P$[32]	CH_3PF_2[33]	PF_3[34]
r(P−C)	184.6(3)	182(2)	
r(P−F)		158.2(f)	157.0(1)
∠CPC	98.6(3)		
∠CPF		97.8(5)	
∠FPF		98.4(5)	97.8(2)

[a] All values are taken from gas-phase electron diffraction studies (r_g/pm, ∠/deg) except with CH_3PF_2, for which r_0 values derived from a microwave study are given. [b] Figures in parentheses are the estimated standard deviations; f = fixed. [c] This work.

Likewise, the estimates of the As−C distance are also in keeping with the expectations of these simple models. The value of r_g(As−C) determined previously for Me_3As is 197.0(3) pm.[10] Replacement of one of the methyl groups by fluorine leads to a shortening of the As−C distance in $(CH_3)_2AsF$ [r_g = 195.5(1) pm] and to a further shortening in CH_3AsF_2 [r_g = 194.9(4) pm]. The As−C distances also invite comparison with those found in $(CH_3)_4As_2$ [r_g = 197.5(2) pm][29] and with the As−C_{eq} bond lengths in the arsenic(V) derivatives $(CH_3)_5As$ [r_g = 197.5(6) pm][30] and $(CH_3)_3AsF_2$ [r_g = 189.9(6) pm].[31]

Although changes in the electronegativity of the substituents are thus found to alter the bond lengths in a predictable manner, the bond angles are much less sensitive to such alterations. Thus, the XAsX angle in $(CH_3)_3As$ (X = C) is virtually identical to that in AsF_3 (X = F). Likewise, the CAsC angle in $(CH_3)_2AsF$ is at 96.9(8)° virtually indistinguishable from the corresponding angle of 96.1(5)° found in $(CH_3)_3As$;[10] the CAsF angle is hardly altered in going from $(CH_3)_2AsF$ to CH_3AsF_2, while the FAsF angle decreases but slightly from CH_3AsF_2 to AsF_3.[9]

A similar pattern holds for the methylphosphines, the structural properties of which are also presented in Table 10.[32−34] Hence, it may be seen that, although the bond lengths respond to changes in substituent in a manner parallelling that found for the arsenic compounds, the FPF angle is insensitive to such changes, the value for CH_3PF_2 being virtually identical with that for the parent molecule PF_3.

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Supporting Information Available: Tables of symmetry coordinates for CH_3AsF_2 and $(CH_3)_2AsF$ (3 pages). Ordering information is given on any current masthead page.

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