The Molecular Structure of Gaseous Trimethylarsenic Difluoride as determined by Electron Diffraction

Anthony J. Downs,* Michael J. Goode, G. Sean McGrady, and Ian A. Steer
Department of Inorganic Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QR
David W. H. Rankin* and Heather E. Robertson
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The structure of gaseous trimethylarsenic difluoride has been determined by electron diffraction using a heated inlet system. The results are consistent with the presence of a single species, the monomer $(CH_3)_3AsF_2$ with freely rotating CH_3 groups occupying the equatorial sites of a framework in the form of a trigonal bipyramid to complete a heavy-atom skeleton with D_{3h} symmetry. Salient structural parameters (r_a) are: r(As–F) 182.0(0.6), r(As–C) 189.7(0.6), and r(C–H) 110.7(1.3); As–C–H 107.9 (1.5)°. Comparisons with the structures of related molecules show that the switch from AsF_5 to $(CH_3)_3AsF_2$, like that from PF_5 to $(CH_3)_3PF_2$, results in the retention of the axial F–E–F unit (E = P or As), but with a significant attenuation of the E–F bond.

Substituted fluorophosphoranes R_nPF_{5-n}, where R is an organic group, have attracted much attention in the past thirty years, with numerous studies aimed at determining how the structures and reactivities of the compounds are influenced by the nature of R and the value of n.[1] Indeed, the structures of the molecules $(CH_3)_nPF_{5-n}$ (n = 0—3), as determined by electron diffraction,[2–4] provided an important test of the valence-shell electron-pair repulsion (VSEPR) model.[5] By contrast, relatively little is known about the corresponding arsoranes R_nAsF_{5-n}. In addition to the molecules AsF_5, which has been characterised structurally,[6] and $As(CH_3)_5$,[7] the only intermediate member of the series $(CH_3)_nAsF_{5-n}$ described to date as being long-lived at ambient temperatures is $(CH_3)_3AsF_2$.[8] Proton and ^{19}F n.m.r.[8,9] and vibrational[8,10] spectra point to a monomeric molecular species both in the solid state and in solution. The spectra are compatible with, but do not prove, a heavy-atom framework conforming to D_{3h} symmetry with the three methyl groups in the equatorial sites and the two fluorine atoms in the axial sites of a trigonal bipyramid centred on the arsenic atom. Although the white solid can be sublimed slowly *in vacuo* at room temperature, it is not possible under these conditions to produce a molecular flux sufficient for electron diffraction measurements. However, the commissioning of a new heated inlet system as an accessory to the Edinburgh gas diffraction apparatus[11] has been exploited to determine the structure of the gaseous molecule. The structure invites comparison, not only with that of the gaseous $(CH_3)_3PF_2$ molecule,[4] but also with those of other phosphorus and arsenic compounds including fluorine or CH_3 groups as substituents.

Experimental

Synthesis.—Trimethylarsenic difluoride has been prepared in the past by the reaction of the corresponding dichloride with aqueous silver fluoride[8] or, better, sodium fluoride in an acetonitrile medium.[10] However, we preferred to take advantage of the clean and virtually quantitative reaction which occurs between trimethylarsine and xenon difluoride[9] [equation (1)].

$$(CH_3)_3As + XeF_2 \xrightarrow{CCl_3F,\ 250\ K} (CH_3)_3AsF_2 + Xe \quad (1)$$

Interaction of the neat reagents is *liable to be explosive*, but can be moderated by using CCl_3F as a diluent and cooling the mixture to 250 K. The preparation was carried out in Teflon-FEP apparatus with poly(tetrafluoroethylene) couplings and needle valves (Production Techniques Ltd.). Trimethylarsine and CCl_3F were co-condensed with XeF_2 (1.38 g, 8.2 mmol) in the proportions $CCl_3F:(CH_3)_3As:XeF_2$ = *ca.* 30:2:1. Warming the mixture to 250 K results in a smooth reaction which could be monitored by the evolution of elemental xenon; warming to room temperature in the final stages encouraged the reaction to proceed to completion. Evaporation of the solvent at 250 K left a white crystalline solid which was purified by sublimation *in vacuo*. The purity of the resulting rhomboid crystals was checked by reference to the ^1H and ^{19}F n.m.r. spectra of a CD_2Cl_2 solution.[9] Trimethylarsenic difluoride free from any impurity detectable by its n.m.r. spectrum was thus produced in 93% yield based on equation (1) and the quantity of XeF_2 consumed. The material was stored in an evacuated Pyrex glass ampoule at room temperature.

Vibrational Spectroscopic Measurements.—I.r. spectra were measured for solid trimethylarsenic difluoride in the form of a mull (with Nujol or hexachlorobutadiene) and for solutions in acetonitrile; the samples were mounted between Polythene rather than alkali halide windows in an effort to prevent reaction with the windows. Spectra in the region 5 000—200

Table 1. Nozzle-to-plate distances, weighting functions, correlation parameters, scale factors, and electron wavelengths

Nozzle-to-plate distance/mm	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation, p/h	Scale factor, k[a]	Electron wavelength/pm[b]
			nm^{-1}					
259.4	2	20	40	144	164	0.4947	0.820(9)	5.693
94.0	4	80	100	300	352	0.3231	0.748(18)	5.693

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

Table 2. Fundamental modes of $(CH_3)_3AsF_2$ assigned on the basis of a molecule with D_{3h} symmetry

Species	Number[a]	Raman (solid)[b] $\Delta\nu$/cm^{-1}	I.r. (solid)[b,c] ν/cm^{-1}	Mode description
a_1'	ν_1	2 940	Inactive	C–H sym. stretch
	ν_2	(1 292)	Inactive	CH_3 sym. deformation
	ν_3	595 (593)	Inactive	As–C sym. stretch
	ν_4	464 (477)	Inactive	As–F sym. stretch
a_2'	ν_5	Inactive	Inactive	C–H antisym. stretch
	ν_6	Inactive	Inactive	CH_3 antisym. deformation
	ν_7	Inactive	Inactive	CH_3 rock
a_2''	ν_8	Inactive	3 007	C–H antisym. stretch
	ν_9	Inactive	1 421	CH_3 antisym. deformation
	ν_{10}	Inactive	910	CH_3 rock
	ν_{11}	Inactive	525 (507)	As–F antisym. stretch
	ν_{12}	Inactive	270 (274)	$As(CH_3)_3$ out-of-plane bend
e'	ν_{13}	3 021	n.o.	C–H antisym. stretch
	ν_{14}	n.o.	2 930	C–H sym. stretch
	ν_{15}	n.o.	1 421	CH_3 antisym. deformation
	ν_{16}	n.o.	1 278	CH_3 sym. deformation
	ν_{17}	n.o.	936, 921	CH_3 rock
	ν_{18}	668 (657)	668,664	As–C antisym. stretch
	ν_{19}	292 (298)	291 (290)	$As(CH_3)_3$ in-plane deformation
	ν_{20}	172 (160)	177	AsF_2 axial bend
e''	ν_{21}	3 021	Inactive	C–H antisym. stretch
	ν_{22}	n.o.	Inactive	CH_3 antisym. deformation
	ν_{23}	n.o.	Inactive	CH_3 rock
	ν_{24}	310 (298)	Inactive	AsF_2 twist

[a] Torsional modes are not included. [b] Values in parentheses refer to solutions of $(CH_3)_3AsF_2$ in CH_3CN. [c] The wavenumbers tally with those reported in ref. 8 with the exception of one of the ν(C–H) modes. n.o. = Not observed.

cm^{-1} were recorded with a Perkin-Elmer 225 spectrophotometer; the region 800—33 cm^{-1} was scanned with a Beckman IR11. Raman spectra of the powdered solid and acetonitrile solutions contained in suitable Pyrex glass cells were excited with the 435.8 nm Hg line of a 3-kW Toronto arc and recorded with a Cary model 81 spectrometer.

Electron-diffraction Measurements.—Electron-scattering patterns were recorded on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus,[11] with nozzle-to-plate distances of *ca.* 94 and 260 mm and an accelerating voltage near 44 kV (electron wavelength *ca.* 5.7 pm). The ampoule containing the sample and intervening glass and stainless-steel pipework were held at *ca.* 328 K with the aid of heating tape, and the vapour was admitted to the diffraction chamber *via* a stainless-steel nozzle the temperature of which (339 K) was controlled by a heated air stream. The precise nozzle-to-plate distances and electron wavelengths (which were determined from scattering patterns for benzene recorded immediately before the sample patterns) are given in Table 1, together with the weighting functions used to set up the off-diagonal weight matrix, the correlation parameters, and final scale factors.

Details of the electron-scattering patterns were accumulated in digital form using a computer-controlled Joyce-Loebl MDM6 microdensitometer with the scanning program described previously.[12] Calculations, performed on ICL 2972 computers at the Edinburgh Regional Computing Centre, made use of the programs for data reduction [12] and least-squares refinement [13] described elsewhere, the complex scattering factors being those listed by Schäfer *et al.*[14]

Results

Structure Refinement.—On the evidence of the ^1H and ^{19}F n.m.r. and vibrational spectra, trimethylarsenic difluoride appears to have a molecular framework derived from a trigonal bipyramid with equatorially sited CH_3 and axially sited F substituents. Thus, the n.m.r. spectra [8,9] of solutions of the compound indicate magnetic equivalence of the two fluorine atoms and of the three methyl groups at ambient temperatures. Details of both the i.r. and Raman spectra appear not to have been published previously, but the number, energies, and activities of the vibrational modes give good grounds for believing that the compound exists in the solid state and in solution in acetonitrile as a symmetrical $(CH_3)_3AsF_2$ molecule conforming to D_{3h} symmetry. The results summarised in Table 2 indicate the extent to which the spectra can be interpreted on the basis of such a model. The spectra have much in common with those of $(CH_3)_3AsCl_2$ [10,15] and the analogous phosphorane $(CH_3)_3PF_2$,[16] both of which have been shown independently to possess molecular structures with D_{3h} symmetry,[4,17] yet differ significantly from those of solid $(CH_3)_3AsBr_2$ [10,15] and $(CH_3)_3AsI_2$ [10] which are more aptly formulated as $[(CH_3)_3AsX]^+X^-$ (X = Br[17] or I).

Accordingly we adopted just such a model as a basis for calculating electron-scattering intensities; local C_{3v} symmetry has been assumed for each of the CH_3 groups and we have explored the effects of twisting the groups about the As–C axes. In all, our model has involved five independent geometrical parameters. With reference to Figure 1, these comprise the three bonded distances *r*(As–F), *r*(As–C), and *r*(C–H), and two angles, *viz.* As–C–H and a CH_3 'twist' angle φ. The orientation of the CH_3 groups is defined in terms of φ such that $\varphi = 0$ corresponds to the situation where one C–H bond of each CH_3 group is coplanar with the AsC_3 skeleton; the three CH_3 groups can then be rotated in a concerted manner about their C_3 axes by the angle φ.

The experimental radial distribution curve (Figure 2) shows prominent, well defined peaks near 110, 185, and 260 pm. Scattering from C–H bonded atom pairs is responsible for the first of these, whereas the contributions of the As–C and As–F bonded atom pairs overlap to give the second, and C$\cdots$F non-bonded atom pairs account for the third. Near 330, 360, and 410 pm there are weaker, more diffuse features representing mainly the scattering from C$\cdots$C, F$\cdots$F, and C$\cdots$H non-bonded atom pairs respectively.

Molecular-scattering intensities have been calculated by established procedures and the molecular structure has been refined on this basis by full-matrix least-squares analysis. In some trial refinements estimated 'shrinkage' corrections were applied to the C$\cdots$C, C$\cdots$F, and F$\cdots$F non-bonded distances, but the effects on the structure analysis were so slight as to be negligible. No corrections have therefore been applied for shrinkage in the final analysis. All five of the geometrical parameters used to define the model have yielded to simultaneous refinement. The initial calculations converged on a value of 0 for the CH_3 'twist' angle φ implying a molecular conformation with C_{3h} symmetry overall. However, a better account of the observed scattering was provided by a model in which the CH_3 groups are assumed to undergo independent free rotation. For this purpose the groups were each represented by a set of 12 hydrogen atoms, each given a weight of $\frac{1}{4}$ and spaced equally around a circle, as shown in Figure 1. Independent refinement has also been accomplished for the amplitudes of vibration associated with the As–F, As–C, and C–H bonded distances on the one hand, and the F$\cdots$F, As$\cdots$H, and C$\cdots$C non-bonded distances on the other. Otherwise we have drawn on the precedents set by the related $(CH_3)_3PF_2$ [4] and $As(CH_3)_3$ [18] to fix reasonable values for the remaining amplitudes.

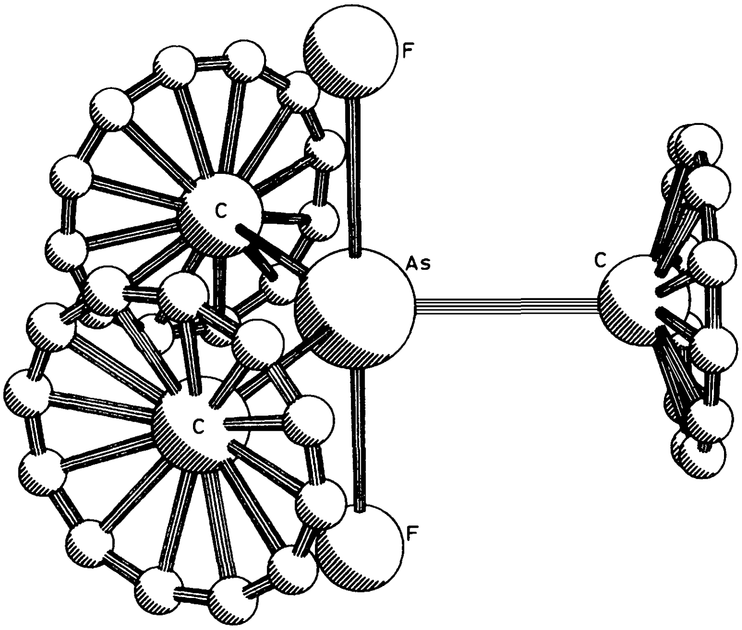

Figure 1. Perspective view of the molecule $(CH_3)_3AsF_2$ illustrating the skeletal geometry and the model used to define the free rotation of the methyl groups

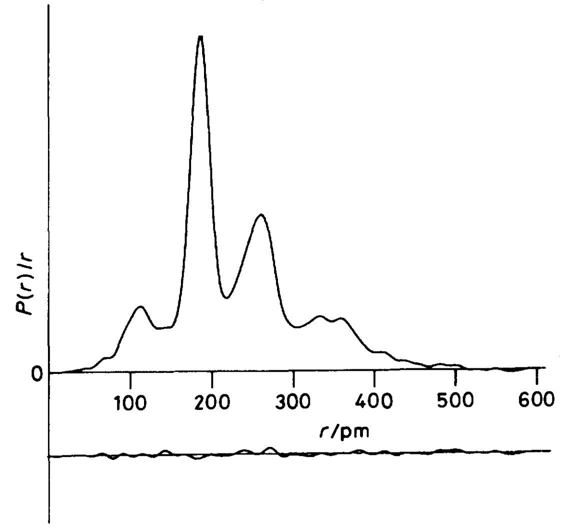

Figure 2. Observed and difference radial distribution curves, $P(r)/r$ *vs.* r, for $(CH_3)_3AsF_2$. Before Fourier transformation the data were multiplied by $s \cdot \exp[(-0.000\,02\,s^2)/(Z_{As} - f_{As})(Z_F - f_F)]$

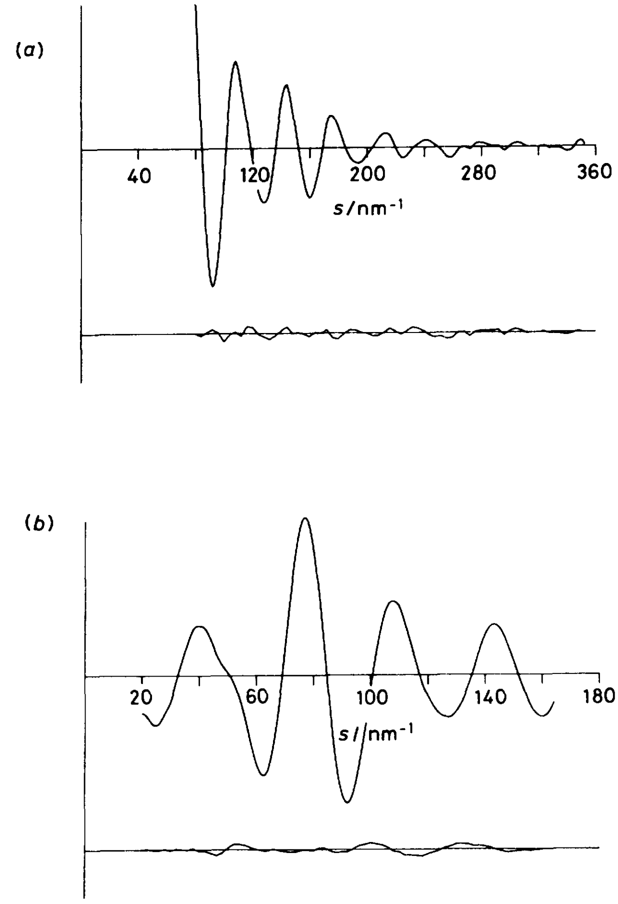

Figure 3. Experimental and final difference molecular-scattering intensity curves for $(CH_3)_3AsF_2$; nozzle-to-plate distances (*a*) 94.0 and (*b*) 259.4 mm

The success of the refinement may be judged overall by reference to the difference between the experimental radial distribution curve and that calculated on the basis of the optimum model (Figure 2). Figure 3 offers a similar comparison between the experimental and calculated molecular scattering. The structural details and vibrational amplitudes of the optimum refinement, corresponding to $R_G = 0.103$ ($R_D = 0.063$), are listed in Table 3. The estimated standard deviations allow for the effects of correlation and have been increased to take account of systematic errors in the electron wavelength, nozzle-to-plate distances, *etc.* Despite appreciable correlation of the parameters defining the As–C and As–F distances and, to a lesser extent, the As–C–H bond angle, as revealed by the portion

Table 3. Molecular parameters for $(CH_3)_3AsF_2$[a]

Parameter	Distance/pm or angle/°	Amplitude/pm
(*a*) Independent parameters		
r_1(As–C)	189.7(0.6)	5.5(0.6)
r_2(As–F)	182.0(0.6)	7.4(0.8)
r_3(C–H)	110.7(1.3)	10.6(1.4)
As–C–H	107.9(1.5)	
(*b*) Dependent distances and amplitudes		
d_4(F ··· F)	364.0(1.2)	7.6(1.5)
d_5(H ··· H)	182.4(2.8)	11.0[b]
d_6(As ··· H)	247.2(1.4)	17.1(1.7)
d_7(C ··· F)	262.9(0.5)	11.0(0.6)
d_8(C ··· C)	328.5(1.0)	13.5(2.1)
d(H ··· F)	237—364	15.0[b]
d(H ··· C)	324—417	15.0[b]
d(H ··· H′)[c]	280—490	20.0[b]

[a] Figures in parentheses are the estimated standard deviations of the last digits. [b] Fixed. [c] H and H′ refer to the hydrogen atoms of *different* methyl groups.

Table 4. Portion of least-squares correlation matrix showing off-diagonal elements greater than 50%

		Vibrational amplitudes		
r(As–F)	As–C–H	u(As–F)	u(As–C)	
−72		−84		r(As–C)
	−50			r(C–H)
		50	64	r(As–F)

Table 5. Dimensions of $(CH_3)_3AsF_2$ and some related methyl and fluoro derivatives of *p*-block elements[a]

Molecule	r(E–F)/pm	r(E–C)/pm	Ref.
PF_5	158.0 (ax) 153.2 (eq)		2
PF_3	157.0		*b*
$(CH_3)_3PF_2$	168.5	181.3	4
$(CH_3)_3P$		184.7	21
AsF_5	171.1 (ax) 165.6 (eq)		6
AsF_3	170.6		6
$(CH_3)_3AsF_2$	182.0	189.7	This work
$(CH_3)_3As$		196.8	18
$(CH_3)_3AsO$		193.7	22
$(CH_3)_3AsS$		194.0	22
SeF_4	177.1 (ax)[c] 168.2 (eq)[c]		26
BrF_3	180.9 (ax) 172.8 (eq)		27
KrF_2	188.9		28

[a] All the results relate to gaseous molecules and have been deduced from electron-diffraction measurements except where indicated otherwise. [b] Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, 1969, **8**, 867. [c] Measured by microwave spectroscopy.

of the least-squares correlation matrix reproduced in Table 4, the main features of the structures are well defined.

Discussion

Our analysis of the electron-diffraction pattern of gaseous trimethylarsenic difluoride leads us first to the conclusion that the compound exists predominantly as monomeric $(CH_3)_3AsF_2$ in the vapour phase at 320—340 K. As expected for a molecule in which the central *p*-block atom has a formal count of 10 electrons in its valence shell, the framework of $(CH_3)_3AsF_2$ has the form of a trigonal bipyramid; the results confirm and extend the inferences drawn from the vibrational spectra, namely that the three methyl groups occupy equatorial sites and the two fluorine atoms axial sites to complete a C_3AsF_2 skeleton with D_{3h} symmetry. This is consistent too with the suggested order of 'apicophilicity' of ligands,[19] F > Cl, Br > CF_3 > OR, SR, NR_2, CH_3, although the molecular structures of certain gaseous phosphoranes appear to argue that the order is not invariant.[20]

The structure of $(CH_3)_3AsF_2$ resembles most obviously that of the phosphorane $(CH_3)_3PF_2$[4] while inviting comparisons also with those of AsF_5[6] and $(CH_3)_3As$.[18] Collation of the dimensions of these and related molecules (Table 5) is revealing for the light it sheds on the effects of changing the character of either the central atom or the substituents. Two features catch the eye.

(*i*) The As–C bond is appreciably shorter in $(CH_3)_3AsF_2$ (189.7 pm) than in the trivalent arsine $(CH_3)_3As$ (196.8 pm).[18] The P–C bond shows a similar change, *viz.* $(CH_3)_3PF_2$ (181.3 pm)[4] and $(CH_3)_3P$ (184.7 pm),[21] but the magnitude of the effect is less than half that exhibited by the corresponding arsenic compounds. Thus, there is a perceptible shortening of the bond to carbon as the oxidation number of the Group 5 atom changes from +3 to +5, with a concomitant increase in its effective electronegativity. In a similar vein, we note that the As–F bonds in the *equatorial* plane of AsF_5 are shorter than those in AsF_3,[6] the proportional change (2.9%) being marginally smaller than that experienced by the As–C bonds in the switch from $(CH_3)_3As$ to $(CH_3)_3AsF_2$ (3.6%). A similar, but also less marked, shortening of the As–C bond accompanies the oxidation of $(CH_3)_3As$ to form the arsenic(V) molecules $(CH_3)_3As{=}X$ (X = O or S), the C_3AsX skeletons of which share the C_{3v} symmetry of the parent molecule; thus, the following As–C bond lengths (in pm) have been reported: $(CH_3)_3As$ 196.8,[18] $(CH_3)_3AsO$ 193.7,[22] and $(CH_3)_3AsS$ 194.0.[22]

(*ii*) Comparison of AsF_5[6] with $(CH_3)_3AsF_2$ shows that the axial As–F bond is attenuated by no less than 10.9 pm as CH_3 replaces F in the equatorial sites. The switch from PF_5[2] to $(CH_3)_3PF_2$[4] is accompanied by a similar attenuation of the axial P–F bond, amounting to 10.5 pm. This effect has been interpreted by VSEPR arguments[5] in terms of the increased repulsions developed by the electron pairs forming the bonds to the less electronegative CH_3 groups. An alternative explanation is offered, however, by simple molecular orbital arguments. As fluorine gives way to methyl as the equatorial substituent, there is a significant reduction in the effective nuclear charge acting on the valence electrons of the Group 5 atom E (= P or As); as illustrated schematically in Figure 4, this results in a poorer energy match between the np_z orbital centred on E and the appropriate a_2'' combination of $2p_z$ orbitals furnished by the axial fluorine atoms, to the detriment of the three-centre four-electron bonding in the axial F–E–F unit.

Whatever the cause may be, gaseous $(CH_3)_3AsF_2$ contains one of the longest As–F bonds to be characterised to date. It is longer than the bonds normally encountered in the $[AsF_6]^-$ anion ($\leqslant$ 178 pm)[23] and is exceeded only by the corresponding bond of an analogous molecule: on the basis of *X*-ray diffraction of a single crystal, a molecular structure has been deduced for Ph_3AsF_2 with an As–F distance of 183.4(0.7) pm.[24] Quite apart from the difficulty of comparing directly interatomic distances deduced from electron diffraction with those deduced from *X*-ray diffraction, it is likely that intermolecular forces will modify slightly but significantly the dimensions of such a molecule in the crystalline state. The behaviour of other

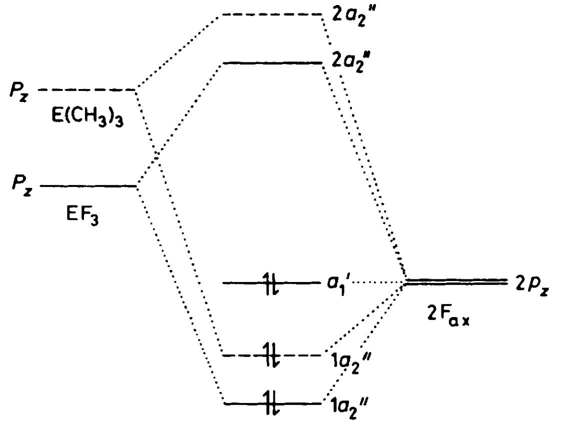

Figure 4. Schematic molecular-orbital energy scheme for the axial F–E–F unit in the molecules EF_5 and $(CH_3)_3EF_2$ (E = P or As)

molecular fluorides suggests that intermolecular binding in the solid state will be partly at the expense of intramolecular As–F binding, so that the move from the vapour to the solid state results in a lengthening of the As–F bonds (*cf.* the bond lengths of 197.9 and 200 pm for XeF_2 in the vapour[25a] and crystalline[25b] phases respectively).

In the VSEPR sense, the molecular $(CH_3)_3AsF_2$ can be compared with KrF_2, the bonding electron pairs engaging the relatively electropositive methyl groups giving way to lone pairs. Just as the molecules PF_5, CH_3PF_4, and $(CH_3)_2PF_3$ emulate in their structures the binary fluorides in the series PF_5, SF_4, and ClF_3,[2–5] so AsF_5 and $(CH_3)_3AsF_2$ reflect the extremes of the series AsF_5, SeF_4, BrF_3, and KrF_2, in which the axial E–F bond length increases with the progressive introduction of lone pairs in the equatorial belt of the central atom, *viz.* 171.1, 177.1, 180.9, and 188.9 pm for E = As,[6] Se,[26], Br,[27] and Kr[28] respectively.

With r(C–H) = 110.7(1.3) pm and As–C–H = 107.9(1.5)°, the CH_3 groups in $(CH_3)_3AsF_2$ have dimensions in line with those in other methyl–metal derivatives[18,29] (*cf.* the methyltitanium compound CH_3TiCl_3[30]). As noted previously, the refinement calculations are consistent with independent free rotation of the three CH_3 groups. This is in keeping with the small barrier to rotation expected for such a structure;[31] it appears also to comply with the behaviour of the analogous phosphorane $(CH_3)_3PF_2$.[4] However, there are some questions which remain unanswered. For example, the torsional motion of the CH_3 groups may not be independent but concerted. Moreover, the model we have employed causes the C–H bonds to move on the surfaces of right vertical cones: in practice, all sorts of distortions may occur as the H atoms of the CH_3 groups pass one another or as they pass the F atoms. The shortest H $\cdots$ H distance is 280 pm, a value large enough to suggest little interaction; by contrast, the H $\cdots$ F distance may be as short as 237 pm, a value less than the sum of the relevant van der Waals radii (*ca.* 267 pm).[32] Curiously the amplitudes of vibration for both the C–H and As $\cdots$ H distances, at 10.6 and 17.1 pm respectively, are larger than expected [*cf.* u(C–H) = 6.3—8.0 pm and $u(E \cdots H)$ = 11.0—14.7 pm for other molecules containing the $(CH_3)_3E$ unit, where E = P, Ga, or As[4,18,21,22,29]]. These may indicate some dynamic distortion of the methyl groups in the $(CH_3)_3AsF_2$ molecule. No detailed analysis of the vibrational spectra has yet been ventured, although the wavenumbers of the features attributable to internal vibrations of the CH_3 groups listed in Table 2 parallel quite closely those of $(CH_3)_3PF_2$[16] and $(CH_3)_3AsCl_2$[15] with no hint of anything untoward. It is noteworthy too that, whereas the vibrational amplitude of the As–C bond in $(CH_3)_3AsF_2$ is, at 5.5 pm, comparable with those of the same bond in $(CH_3)_3As$ (6.2 pm),[18] $(CH_3)_3AsO$ (5.7 pm),[22] and $(CH_3)_3AsS$ (5.1 pm),[22] the amplitude of the As–F bond is, at 7.4 pm, appreciably greater than those of the same bond in AsF_5 (5.2 pm, but assumed)[6] and of the corresponding bonds in SeF_4 (4.5 pm),[33] BrF_3 (5.0 pm),[27] and KrF_2 (5.2 pm).[28] Yow and Bartell[4] have remarked that the lengthening of the axial P–F bonds in the series PF_5, CH_3PF_4, $(CH_3)_2PF_3$, $(CH_3)_3PF_2$ correlates well with the increase in amplitude of vibration, although the magnitude of the change (4.3—4.8 pm) is barely outside the limits of error and is in any case clouded by the effects of correlation between the equatorial and axial bonded distances.[2–4,6] Analysis of the electron-diffraction pattern of AsF_5 also ran into difficulty hereabouts,[6] convergence occurring at what was judged to be an 'unreasonably large' amplitude for the bonded As–F distances. In these circumstances, therefore, it would be a mistake to read too much into the As–F amplitude deduced from our final analysis. There is clearly more work to be done on the vibrational properties of the gaseous or matrix-isolated $(CH_3)_3AsF_2$ molecule if more definitive conclusions are to be sought.

Acknowledgements

We thank the S.E.R.C. for research grants and the award of research studentships (to M. J. G. and I. A. S.).

References

1 See for example, R. Schmutzler, in 'Halogen Chemistry,' ed. V. Gutmann, Academic Press, New York, 1967, vol. 2, p. 31.
2 K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, 1965, **4**, 1775; H. Kurimura, S. Yamamoto, T. Egawa, and K. Kuchitsu, *J. Mol. Struct.*, 1986, **140**, 79.
3 L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, 1965, **4**, 1777.
4 H. Yow and L. S. Bartell, *J. Mol. Struct.*, 1973, **15**, 209.
5 R. J. Gillespie, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 819; 'Molecular Geometry,' van Nostrand Reinhold, London, 1972.
6 F. B. Clippard, jun., and L. S. Bartell, *Inorg. Chem.*, 1970, **9**, 805.
7 K-H. Mitschke and H. Schmidbaur, *Chem. Ber.*, 1973, **106**, 3645.
8 M. H. O'Brien, G. O. Doak, and G. G. Long, *Inorg. Chim. Acta*, 1967, **1**, 34.
9 A. M. Forster and A. J. Downs, *Polyhedron*, 1985, **4**, 1625.
10 I. A. Steer, D.Phil. Thesis, University of Oxford, 1969.
11 C. M. Huntley, G. S. Laurenson, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1980, 954.
12 S. Cradock, J. Koprowski, and D. W. H. Rankin, *J. Mol. Struct.*, 1981, **77**, 113.
13 A. S. F. Boyd, G. S. Laurenson, and D. W. H. Rankin, *J. Mol. Struct.*, 1981, **71**, 217.
14 L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, 1971, **55**, 3055.
15 C. Woods and G. G. Long, *J. Mol. Spectrosc.*, 1971, **40**, 435.
16 A. J. Downs and R. Schmutzler, *Spectrochim. Acta, Part A*, 1967, **23**, 681.
17 M. B. Hursthouse and I. A. Steer, *J. Organomet. Chem.*, 1971, **27**, C11.
18 R. Blom, A. Haaland, and R. Seip, *Acta Chem. Scand., Ser. A*, 1983, **37**, 595; B. Beagley and A. R. Medwid, *J. Mol. Struct.*, 1977, **38**, 229.
19 I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Acc. Chem. Res.*, 1971, **4**, 288; R. G. Cavell, D. D. Poulin, K. I. The, and A. J. Tomlinson, *J. Chem. Soc., Chem. Commun.*, 1974, 19; R. G. Cavell, J. A. Gibson, and K. I. The, *J. Am. Chem. Soc.*, 1977, **99**, 7841.
20 H. Oberhammer and J. Grobe, *Z. Naturforsch., Teil B*, 1975, **30**, 506; H. Oberhammer, J. Grobe, and D. LeVan, *Inorg. Chem.*, 1982, **21**, 275.
21 L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, 1960, **32**, 512.
22 C. J. Wilkins, K. Hagen, L. Hedberg, Q. Shen, and K. Hedberg, *J. Am. Chem. Soc.*, 1975, **97**, 6352.
23 See for example, R. F. Copeland, S. H. Conner, and E. A. Meyers, *J. Phys. Chem.*, 1966, **70**, 1288; G. Gafner and G. J. Kruger, *Acta Crystallogr., Sect. B*, 1974, **30**, 250.
24 A. Augustine, G. Ferguson, and F. C. March, *Can. J. Chem.*, 1975, **53**, 1647.

25 (*a*) N. J. Brassington, H. G. M. Edwards, and D. A. Long, *J. Chem. Soc., Faraday Trans. 2*, 1978, 1208; (*b*) H. A. Levy and P. A. Agron, *J. Am. Chem. Soc.*, 1963, **85**, 241; in 'Noble-Gas Compounds,' ed. H. H. Hyman, The University of Chicago Press, Chicago and London, 1963, p. 221.

26 I. C. Bowater, R. D. Brown, and F. R. Burden, *J. Mol. Spectrosc.*, 1968, **28**, 454.

27 A. A. Ishchenko, I. N. Myakshin, G. V. Romanov, V. P. Spiridonov, and V. F. Sukhoverkhov, *Dokl. Akad. Nauk SSSR*, 1982, **267**, 1143.

28 W. Harshbarger, R. K. Bohn, and S. H. Bauer, *J. Am. Chem. Soc.*, 1967, **89**, 6466.

29 See for example, A. Almenningen, A. Haaland, and G. L. Morgan, *Acta Chem. Scand.*, 1969, **23**, 2921; A. Almenningen, S. Halvorsen, and A. Haaland, *ibid.*, 1971, **25**, 1937; B. Beagley, D. G. Schmidling, and I. A. Steer, *J. Mol. Struct.*, 1974, **21**, 437; M. T. Barlow, A. J. Downs, P. D. P. Thomas, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1979, 1793; M. T. Barlow, C. J. Dain, A. J. Downs, P. D. P. Thomas, and D. W. H. Rankin, *ibid.*, 1980, 1374; H. Günther, H. Oberhammer, and R. Eujen, *J. Mol. Struct.*, 1980, **64**, 249; T. Fjeldberg, A. Haaland, R. Seip, Q. Shen, and J. Weidlein, *Acta Chem. Scand., Ser. A*, 1982, **36**, 495.

30 A. Berry, Z. Dawoodi, A. E. Derome, J. M. Dickinson, A. J. Downs, J. C. Green, M. L. H. Green, P. M. Hare, M. P. Payne, D. W. H. Rankin, and H. E. Robertson, *J. Chem. Soc., Chem. Commun.*, 1986, 520.

31 See for example, E. Tannenbaum, R. Myers, and W. Gwinn, *J. Chem. Phys.*, 1956, **25**, 42; R. E. Naylor, jun., and E. B. Wilson, jun., *ibid.*, 1957, **26**, 1057.

32 W. W. Porterfield, 'Inorganic Chemistry: a Unified Approach,' Addison-Wesley Publishing Co. Inc., Reading, Massachusetts, 1984, p. 168.

33 E. J. Baran, *Monatsh. Chem.*, 1981, **112**, 301.

Received 20*th February* 1987; *Paper* 7/322