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QUANTITATIVE SYNTHESIS OF  $(C_6H_5)_2AsF_2 + AsF_6$ -AND  $(C_6H_5)_2AsF_3$  VIA INTERACTION OF BENZENE WITH ARSENIC PENTAFLUORIDE

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### Authors

Tanzella, F.L.  
Bartlett, N.

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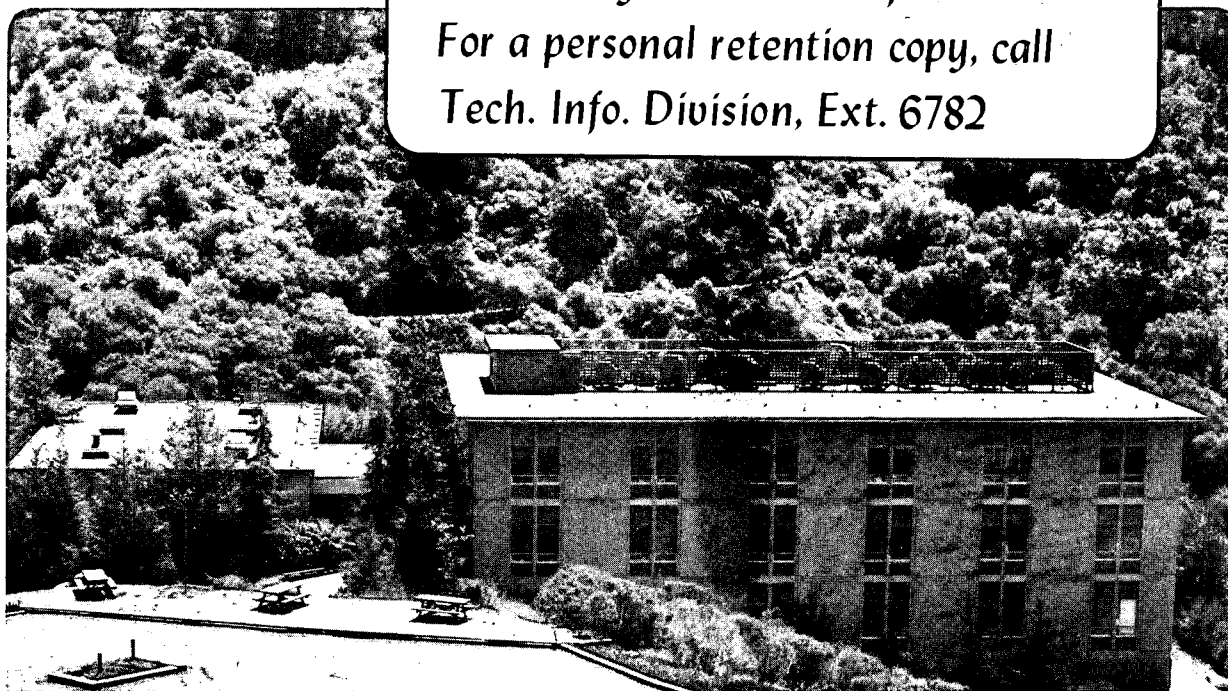
QUANTITATIVE SYNTHESIS OF  $(C_6H_5)_2AsF_2^+AsF_6^-$  AND  
 $(C_6H_5)_2AsF_3$  VIA INTERACTION OF BENZENE WITH ARSENIC  
PENTAFLUORIDE

Francis L. Tanzella and Neil Bartlett

May 1981

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Quantitative Synthesis of  $(C_6H_5)_2AsF_2^+AsF_6^-$  and  
 $(C_6H_5)_2AsF_3$  via Interaction of Benzene with Arsenic  
Pentafluoride.

Quantitative Synthese von  $(C_6H_5)_2AsF_2^+AsF_6^-$  und  
 $(C_6H_5)_2AsF_3$  durch Reaktion von Benzol mit Arsenpentafluorid

By Francis L. Tanzella and Neil Bartlett\*

Department of Chemistry, University of California and the  
Materials and Molecular Research Division, Lawrence Berkeley  
Laboratory, Berkeley, California 94720 (U.S.A.)

A contribution to honor Professor Dr. Oskar Glemser on the  
occasion of his 70th birthday.

\* Reprint requests to Prof. Dr. N. Bartlett

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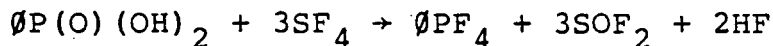
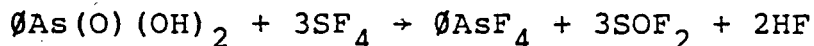
#### ABSTRACT

Benzene reacts quantitatively with  $\text{AsF}_5$  to give  $(\text{C}_6\text{H}_5)_2\text{AsF}_2^+\text{AsF}_6^-$ , the first reported aryl or alkyl fluoroarsonium(V) salt. This reacts quantitatively with  $\text{CsF}$  to give  $(\text{C}_6\text{H}_5)_2\text{AsF}_3$  and  $\text{CsAsF}_6$ . Interaction of  $(\text{C}_6\text{H}_5)_2\text{AsF}_3$  with  $\text{AsF}_5$  reconstitutes the fluoroarsonium salt. Variable temperature  $^{19}\text{F}$  NMR studies show  $\text{C}_6\text{H}_5_2\text{AsF}_3$  to be a rigid trigonal bipyramid, with the phenyl groups in equatorial positions, to  $71^\circ\text{C}$ .

### Introduction

The reaction of benzene with  $O_2^+AsF_6^-$  or  $C_6F_6^+AsF_6^-$  gives a mixture of products<sup>1</sup>. In order to clarify that chemistry, the reaction of  $C_6H_6$  with  $AsF_5$  was undertaken on the assumption that the reactions with  $O_2AsF_6$  and  $C_6F_6AsF_6$  generated some  $AsF_5$  which could also interact with benzene.

No products have heretofore been reported for the reaction of  $C_6H_6$  with either  $PF_5$ ,  $AsF_5$  or  $SbF_5$ , although  $C_6H_5AsF_4$  and  $C_6H_5PF_4$  have each been synthesized<sup>2,3</sup> by other routes:

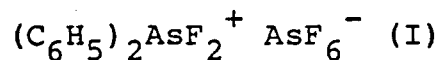


When  $AsF_5$  is passed into a solution of  $C_6H_6$  in either HF or  $SO_2ClF$  a white crystalline product forms quickly and quantitatively. This is identical to one of the products from  $O_2^+$  or  $C_6F_6^+$  salt interactions with benzene. The physical and chemical evidence shows that it is the salt  $(C_6H_5)_2AsF_2^+AsF_6^-$ .

### Experimental

General experimental procedures are similar to those described in a related paper.<sup>1</sup> The acquisition and preparation of reagents and solvents are also as described in that paper with the following additions: (C<sub>6</sub>H<sub>5</sub>AsOOH, supplied by Research Organic/Inorganic (Sun Valley, California) was recrystallized from CCl<sub>4</sub>. CsF was used as received from Alfa Ventron (Beverly, Massachusetts). (CH<sub>3</sub>)<sub>2</sub>SO, supplied by Matheson, Coleman and Bell (Norwood, Ohio), was dried and stored over molecular sieves.

### Interaction of benzene with arsenic pentafluoride to give



Arsenic pentafluoride (6.22 mmole, measured tensimetrically) was condensed into a Kel-F tube provided

with a magnetic spinbar and subsequently  $\text{SO}_2\text{ClF}$  (5 ml) was condensed (from its purification vessel held at  $-45^\circ$ ). a molar excess of benzene was condensed on to the frozen solvent. With the bottom half of the tube held at  $-78^\circ$  the benzene in the upper half was allowed to melt at room temperature forming a green color upon solution. This was, (within a few seconds), followed by the formation of a copious colorless precipitate. To ensure completion of the reaction, the tube was held at  $0^\circ$  (with stirring) for one hour. Removal of solvent and drying under vacuum gave a white free-flowing crystalline solid, (1.41 g, 6.2 mmole " $\text{C}_6\text{H}_5\text{AsF}_4$ ")

Analysis Calcd for  $\text{C}_6\text{H}_5\text{AsF}_4$ : C, 31.60; H, 2.21; As, 32.9; F, 33.3%. Found: C, 31.77; H, 2.33; As, 33.1; F, 32.9%. The  $^{19}\text{F}$  NMR spectrum (DMSO) is shown in Figure 1. IR: (Nujol Mull,  $\text{cm}^{-1}$ ) 1575(w), 1342(w), 1272(w), 1185(w), 1078(w), 1065(m), 995(m), 742(s), 709(s), 675(s), 462(m), 398(m), 380(m). The mass spectrum of the volatiles from the solid at  $125^\circ$  showed the  $\text{C}_{12}\text{H}_{10}\text{AsF}_2^+$  species to be the highest molecular weight fragment and of high abundance. X-ray powder and precession data are given in Table 1. The NMR and infrared data support the formulation  $(\text{C}_6\text{H}_5)_2\text{AsF}_2^+\text{AsF}_6^-$  for the solid. This was confirmed by the following chemistry.



Interaction of  $(C_6H_5)_2AsF_2^+ AsF_6^-$  with CsF to give  $(C_6H_5)_2AsF_3$  (II)

$(C_6H_5)_2AsF_2^+ AsF_6^-$  (0.46 g, 1 mmole) from above was mixed with cesium fluoride (0.15 g, 1 mmole) in a Teflon tube. Anhydrous hydrogen fluoride (5 ml) was distilled on to the solids, and the mixture allowed to stand at room temperature for one hour, after which the solvent was removed under vacuum. The resultant white solid was transferred to a Teflon filtration apparatus and extracted with several batches of dry toluene. Removal of the toluene from the filtrate, under vacuum, gave a colorless solid (0.29 g, 1.0 mmole). The  $^{19}F$  NMR spectrum (toluene) is given in Table 1.

Mass spectrum: m/e 286 (4.2)  $\emptyset_2AsF_3^+$ , 264 (24.3)  $\emptyset_2AsF_2^+$ , 248 (5.0)  $\emptyset_2AsF^+$ , 227 (1.6)  $(C_6H_4)_2As^+$ , 209 (11.0)  $\emptyset AsF_3^+$ , 190 (36.5)  $\emptyset AsF_2^+$ , 171 (14.8)  $\emptyset AsF^+$ . The toluene-insoluble by-product of the reaction was shown to be  $CsAsF_6$  by its characteristic X-ray powder pattern.

Interaction of  $(C_6H_5)_2AsF_3$  with  $AsF_5$

$(C_6H_5)_2AsF_3$  (0.210 g, 0.73 mmole), obtained as described above, was placed in a Teflon tube and anhydrous hydrogen fluoride (5 ml) condensed on top of it. A molar excess of  $AsF_5$  was condensed into the tube and the vessel

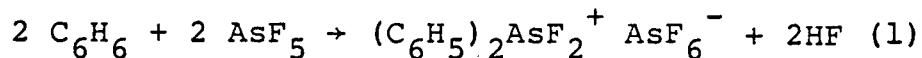
was warmed to room temperature. The solid dissolved and the supply of  $\text{AsF}_5$  was maintained until uptake ceased. The excess of  $\text{AsF}_5$  was removed under vacuum at  $-78^\circ$  and the solvent at room temperature to give a colorless solid (0.331 g, 0.73 mmole). An X-ray powder pattern of this product was identical to that obtained from the benzene/ $\text{AsF}_5$  reaction.

#### Interaction of $(\text{C}_6\text{H}_5)_2\text{AsOOH}$ with $\text{SF}_4$

$\text{SF}_4$  (9.2 g, 85 mmoles) was condensed on to  $(\text{C}_6\text{H}_5)_2\text{AsOOH}$  (4.4 g, 17 mmoles) in a Monel bomb. After being heated at  $200^\circ$  for 12 hours, the solid grey-colored product was placed in a 50 ml flask with 4 g of NaF. The product was dissolved in 20 ml petroleum ether, filtered and recrystallized to give colorless crystalline  $(\text{C}_6\text{H}_5)_2\text{AsF}_3$  (2 g, 7 mmoles). The solid which melts with decomposition  $\sim 135^\circ$ , gives the same mass spectrum and  $^{19}\text{F}$  NMR as described for II above. The NMR was unchanged in the temperature range  $-50^\circ$  to  $+71^\circ$  (see Table 1).

#### Results and Discussion

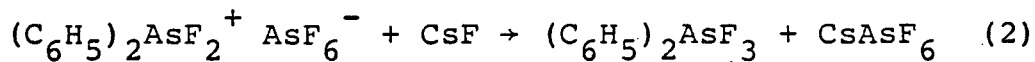
Benzene reacts with Arsenic pentafluoride to give the colorless, crystalline solid  $(\text{C}_6\text{H}_5)_2\text{AsF}_2^+ \text{AsF}_6^-$  (I) in quantitative yield:



## I

I is a non-volatile solid that melts with decomposition at  $\sim 150^\circ$  and the analytical data indicate an empirical formula  $\text{C}_6\text{H}_5\text{AsF}_4$ . However,  $\emptyset\text{AsF}_4$  is reported<sup>2</sup> to be a yellow liquid at ordinary temperatures. The  $^{19}\text{F}$  NMR spectrum (in DMSO with  $\text{CFCl}_3$  as reference) is given in Figure 1. The quartet at  $-61.7$  ppm is characteristic<sup>4</sup> of  $\text{AsF}_6^-$  and the singlet of one-third the intensity at  $-62.8$  ppm suggests the cation  $\emptyset_2\text{AsF}_2^+$ . The shifts are independent of concentration. The mass spectrum obtained from the decomposition of I in the sample chamber of the mass spectrometer shows peaks at  $m/e$  corresponding to  $\emptyset_2\text{AsF}_2^+$ ,  $\emptyset_2\text{AsF}^+$ ,  $(\text{C}_6\text{H}_4)\text{As}^+$ ,  $\emptyset\text{AsF}_2^+$  and  $\text{AsF}_2^+$ . This evidence all indicates the formulation  $(\text{C}_6\text{H}_5)_2\text{AsF}_2^+ \text{AsF}_6^-$ .

In order to characterize I chemically, the arsonium salt was reacted with  $\text{CsF}$ :



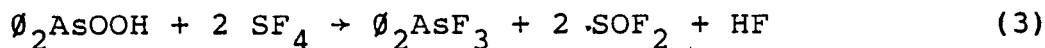
## II

Reaction (2) gives II in quantitative yield. This has the same  $^{19}\text{F}$  NMR spectrum (see Table 1) as that reported by Muetterties<sup>5</sup> for  $\emptyset_2\text{AsF}_3$ . The mass spectrum has ( $m/e$ )

peaks corresponding to  $\text{O}_2\text{AsF}_3$ ,  $\text{O}_2\text{AsF}_2^+$ ,  $\text{O}_2\text{AsF}^+$ ,  $(\text{C}_6\text{H}_4)\text{As}^+$ ,  $\text{OAsF}_3$ ,  $\text{OAsF}_2^+$  and  $\text{OAsF}^+$  as well as some smaller fragments. II is soluble in aromatic solvents and deliquesces quickly in moist air. Although these results are consistent with the formulation  $(\text{C}_6\text{H}_5)_2\text{AsF}_3$ , a small controversy in the literature prevented definite verification.

Littlefield and Doak<sup>6</sup> questioned the published  $^{19}\text{F}$  NMR spectrum. Muetterties had reported<sup>5</sup> that the spectrum for  $\text{O}_2\text{AsF}_3$  consisted of a doublet and triplet of relative intensity 2:1 with a common coupling constant of 67 Hz, suggesting a rigid trigonal bipyramid at room temperature. Littlefield and Doak fluorinated  $\text{O}_2\text{AsH}$  or  $\text{O}_2\text{AsCl}$  with  $\text{SF}_4$  to obtain a crystalline solid the  $^{19}\text{F}$  NMR of which consisted of a singlet (at 69.1 ppm upfield of  $\text{CFCl}_3$ ) relatively unchanged from  $-90^\circ$  to room temperature. On the basis of elemental analyses this material was described as  $\text{O}_2\text{AsF}_3$  and the  $^{19}\text{F}$  NMR findings were attributed to pseudo-rotation. In order to settle this controversy Muetterties' original preparation was repeated.

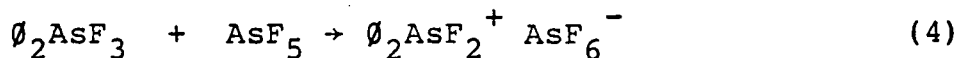
The reaction<sup>7</sup>:



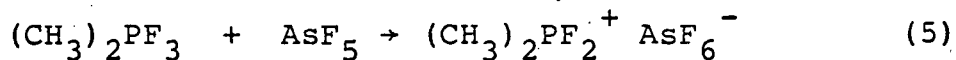
was run using a large excess of  $\text{SF}_4$  in a Monel bomb. The crystalline product (approximately 40% yield) gave a mass

spectrum identical to the one reported for II above. The  $^{19}\text{F}$  NMR spectrum in toluene (see Table 1) consisted of a doublet and a triplet of relative intensity 2:1 with a coupling constant of 70 Hz. The spectrum showed no sign of coalescence in the temperature range  $-50^\circ$  to  $71^\circ$ . This spectrum is identical with that of II. This leaves no doubt of the correctness of the original  $^{19}\text{F}$  NMR studies of Muetterties and their interpretation. Evidently, Littlefield and Doak did not have  $\text{O}_2\text{AsF}_3$  as they thought. Perhaps, because they derived their so-called  $(\text{C}_6\text{H}_5)_2\text{AsF}_3$  from arsenic(III) species ( $\text{O}_2\text{AsH}$  or  $\text{O}_2\text{AsCl}$ ), they may not have produced an arsenic(V) material.

To further the chemical characterization of  $\text{O}_2\text{AsF}_3$ , it was treated with  $\text{AsF}_5$  and this resulted in an alternative synthesis of I:



Brownstein and Schmutzler<sup>8</sup> have reported a similar reaction:

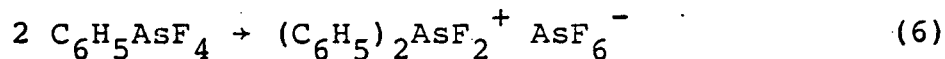


III

where III was identified by its  $^{19}\text{F}$  NMR spectrum but not isolated. These spectroscopic and chemical studies serve to fully characterize the reaction of benzene with  $\text{AsF}_5$ .

Having identified I as the crystalline component in the mixture resulting from the reaction of benzene with either  $O_2^+$  or  $C_6F_6^+$ , the solubility of this salt in a variety of solvents was examined. It was found to be very soluble in anhydrous HF at room temperature. Large needle-shaped crystallites were formed on cooling solutions to  $-78^\circ$ .

Since  $C_6H_5AsF_4$  is not observed in the product of the interaction of benzene with  $AsF_5$  and since Smith<sup>2</sup> did not report I in the synthesis of  $\emptyset AsF_4$ , it seems unlikely that reaction (1) proceeds via a  $\emptyset AsF_4$  intermediate:

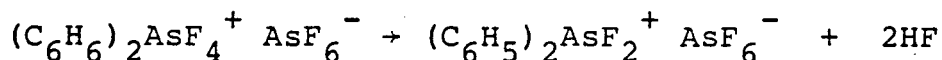
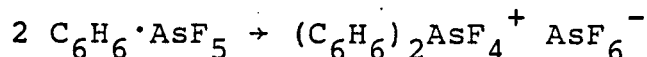
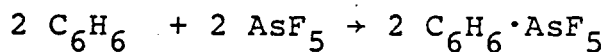


Although some by-product or impurity in the  $C_6H_6/AsF_5$  reaction might catalyze the above disproportionation, Smith has shown  $\emptyset AsF_4$  to be stable in the presence of both  $C_6H_6$  and HF.

Another possible route for the  $C_6H_6/AsF_5$  reaction is via reaction (4) with  $\emptyset_2AsF_3$  as intermediate. However, since no  $\emptyset_2AsF_3$  was seen in reaction (1) even when a ten-fold excess of benzene over  $AsF_5$  was used this reaction route seems unlikely.

A plausible mechanism for the production of I is via the formation of  $C_6H_6 \cdot AsF_5$  adduct followed by dismutation

and HF elimination, the last two processes perhaps occurring concertedly.



It has been suggested from conductivity measurements<sup>9</sup> that the  $\text{CH}_3\text{CN} \cdot \text{AsF}_5$  adduct dismutates to give  $(\text{CH}_3\text{CN})_2\text{AsF}_4^+ \text{AsF}_6^-$ . HF elimination products from this cation have not been seen but the elimination of HF from such a cation may be less likely as the protons of the  $\text{CH}_3$  group are further from the F atoms of the  $\text{AsF}_5$  entity than in the benzene/ $\text{AsF}_5$  case.

Reactions (1) and (2) can be used as a quantitative route for the synthesis of  $\text{C}_6\text{H}_5\text{AsF}_3$  (100% yield based on benzene, 50% yield based on  $\text{AsF}_5$ ). When compared to the 40% yield from the high pressure and temperature method of reaction (3) this new route seems to be a better general method for the clean synthesis of  $\text{C}_6\text{H}_5\text{AsF}_3$ . In fact, other organic molecules may react with  $\text{AsF}_5$  in a similar manner to give the synthesis of various types of  $\text{R}_2\text{AsF}_3$  molecules. Furthermore it is possible that  $\text{PF}_5$  and  $\text{SbF}_5$  may also react

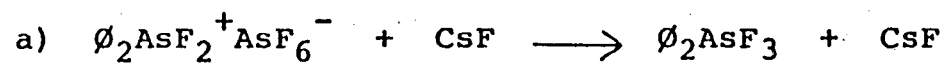
in a similar manner to provide a method for the efficient syntheses of  $R_2PF_3$  and  $R_2SbF_3$  species. Therefore this route based on reactions (1) and (2) could possibly be a general method for the synthesis of pentasubstituted group V compounds of the type  $R_2MF_3$ .

#### Acknowledgements

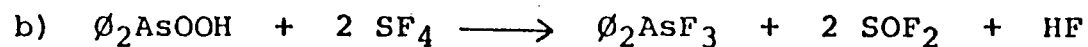
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Table 1.  $^{19}\text{F}$  NMR of  $(\text{C}_6\text{H}_5)_2\text{AsF}_3$



Shift <sup>a</sup>	Multiplicity ( $J_{\text{F-F}}$ )	Integration	Assignment
-69.8	doublet (71 Hz)	2	F <sub>axial</sub>
-92.4	triplet (71 Hz)	1	F <sub>equatorial</sub>

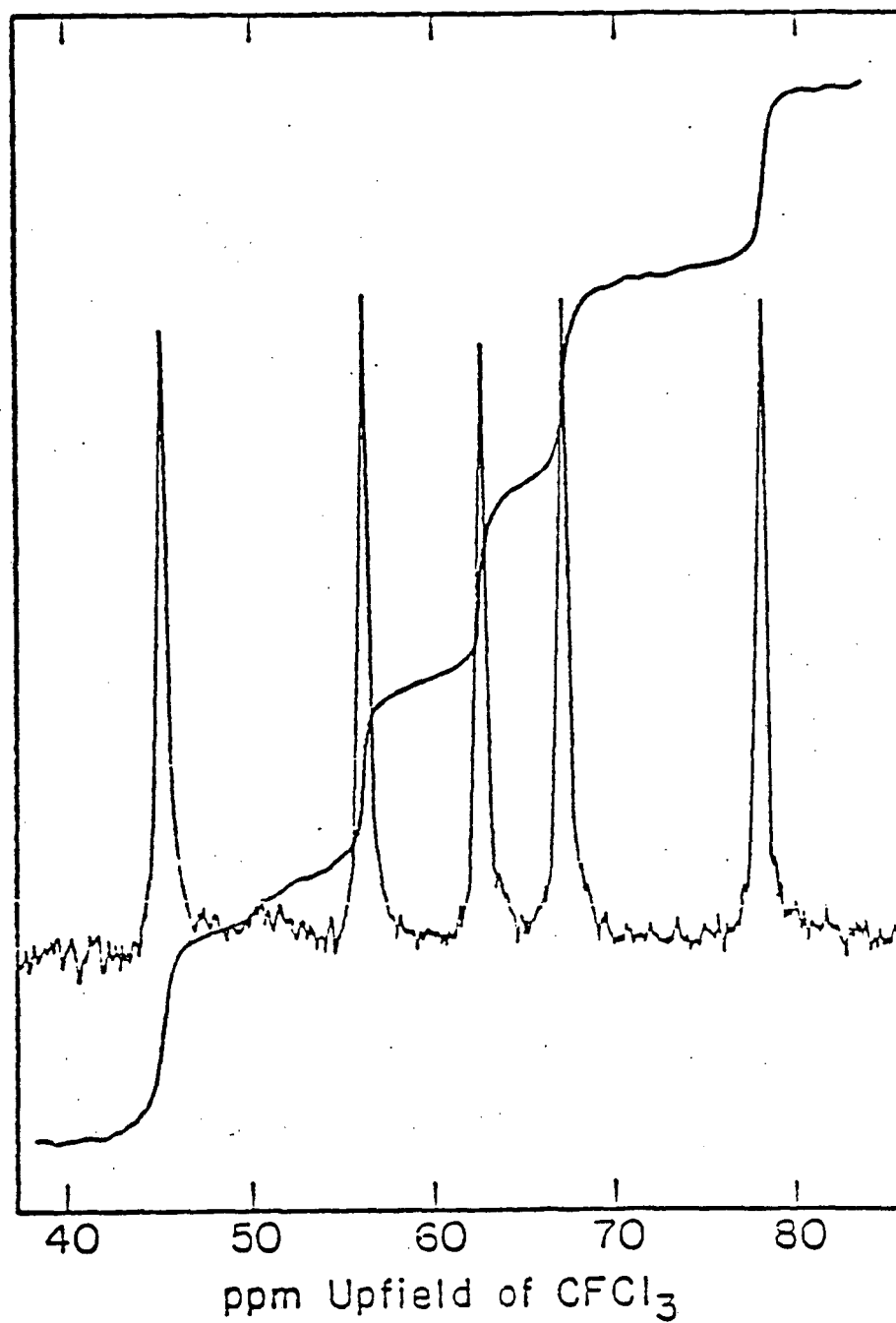


Shift <sup>a</sup>	Multiplicity ( $J_{\text{F-F}}$ )	Integration	Assignment
-70.0	doublet (72 Hz)	2	F <sub>axial</sub>
-92.5	triplet (72 Hz)	1	F <sub>equatorial</sub>

c) Variable Temperature NMR data for b)

Temperature	Shift <sup>a</sup> (F <sub>axial</sub> )	Shift <sup>a</sup> (F <sub>equatorial</sub> )	$J_{\text{F}_a-\text{F}_e}$ (Hz)
-50	-72.0	-91.8	72
0	-70.7	-92.4	72
31	-70.1	-92.6	72
40	-70.0	-92.6	70
50	-69.9	-92.6	69
61	-69.6	-92.8	59
71	-69.5	-92.8	48

a) Negative sign refers to ppm upfield of  $\text{CFCl}_3$ .



Shift	Multiplicity	Integration	Assignment
-61.7	equal intensity quartet (930Hz)	3	$\text{AsF}_6^-$
-62.8	singlet	1	$\text{O}_2\text{AsF}_2^+$

Figure 1.  $^{19}\text{F}$  NMR Spectrum of  $(\text{C}_6\text{H}_5)_2\text{AsF}_2^+\text{AsF}_6^-$

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