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The Preparation and Characterization of Radical-Cation Salts
Derived from Perfluorobenzene, Perfluorotoluene and Perfluoronaphthalene

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Abstract

The salts $C_6F_6^+AsF_6^-$ (yellow), $C_6F_5CF_3^+AsF_6^-$ (lime green), and $C_{10}F_8^+AsF_6^-$ (dark green) may be prepared by electron-oxidation of the appropriate perfluoro-aromatic molecule using $O_2^+AsF_6^-$. Other O_2^+ salts can be similarly employed as can the more strongly oxidizing transition-metal hexafluorides, but salts of the latter are more labile than their AsF_6^- relatives. $C_6F_6^+AsF_6^-$ is a convenient electron-oxidizer ($C_6F_6AsF_6 + C_{10}F_8 \rightarrow C_{10}F_8AsF_6 + C_6F_6$) since that remaining from reaction decomposes at room temperature to volatile products ($2C_6F_6AsF_6 \rightarrow C_6F_6 + 1,4-C_6F_8 + 2AsF_5$). Magnetic susceptibilities for $C_6F_6AsF_6$ and $C_{10}F_8AsF_6$ approximate to Curie law behavior and g values are close to free-electron values. X-ray diffraction data (single crystal) show $C_6F_6AsF_6$ to be primitive rhombohedral with $a_0 = 6.60(1)\text{\AA}$, $\alpha = 106.0(1)^\circ$, $V = 246.1\text{\AA}^3$, $Z = 1$, probable space group $R\bar{3}$, and (powder data) $C_{10}F_8AsF_6$ to be tetragonal with $a_0 = 8.27(5)$; $c_0 = 18.57(s)\text{\AA}$, $V = 1270\text{\AA}^3$, $Z = 4$. Salts derived from the monocyclic perfluoro-aromatics are thermally unstable but can be kept below -15° . The perfluoronaphthalene salts are indefinitely stable at room temperatures. All hydrolyse rapidly. The products of thermal decomposition of the hexafluoroarsenates of the monocyclic-cation salts parallel

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the products of the attack by F^- . The latter reaction products are in the molar ratios indicated by the equations: $2 C_6F_6^+ + 2 F^- \rightarrow C_6F_6 + 1,4-C_6F_8$; $2 C_6F_5 CF_3^+ + 2 F^- \rightarrow C_6F_5 CF_3 + 1,3-C_6F_7 CF_3$. The 1,3- $C_6F_7 CF_3$ isomerises to a 1:1 mixture with 1,4- $C_6F_7 CF_3$ over several days in the presence of fluoroacids. Mechanisms for the formation of the dienes are discussed.

Introduction

Radical cations derived from perfluoro-aromatic molecules were first described by Bazhin et al^{1,2}. The species were made in super acid or oleum solutions and were unambiguously characterized by e.s.r. spectroscopy¹⁻⁵. Such species have also been proposed as intermediates in the oxidative fluorination of aromatic molecules by high valent metal fluorides⁶ such as cobalt trifluoride, by bromine trifluoride⁷ and by xenon difluoride⁸. They have also been invoked in the electrochemical fluorination⁹ of aromatic molecules in the presence of F^- . Salts of such radical-cation species were unknown prior to the synthesis of $C_6F_6^+ AsF_6^-$ in these laboratories^{10,11}.

An earlier attempt by Jha¹² to prepare $C_6F_6^+ PtF_6^-$ from C_6F_6 and PtF_6 yielded a promising orange-yellow solid at low temperatures. A similar material obtained¹¹ using IrF_6 , decomposed well below 0°C. Kinetically stable salts sufficiently stable to be manipulated at room temperatures were first obtained^{10,11} by exploiting dioxygenyl salts as oxidizers:



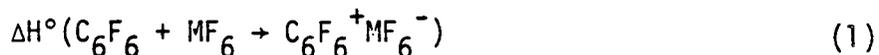
The range of salts has been extended since the preliminary report¹⁰. Utilization of the low melting solvent SO_2ClF has improved yields and provided access to less thermally stable perfluoro-aromatic radical-cation salts. Less powerful oxidizers than O_2^+ salts are needed for the synthesis of $\text{C}_{10}\text{F}_8^+$ and polycyclic-cation salts which have much higher thermal stability than their monocyclic relatives. The preparation and characterization of monocation salts derived from C_6F_6 , $\text{C}_6\text{F}_5\text{CF}_3$ and C_{10}F_8 is reported here. The preparation and some properties of the pentafluoropyridine radical-cation salts have been described elsewhere¹³.

Particular attention has been given to the products of thermal decomposition of the radical-cation salts and the products of F^- attack, since the sets of products are related. Salts of the single-ring aromatics are thermally unstable at room temperature but can be kept below 258K. Their thermal decomposition gives an equimolecular mixture of the parent fluoro-aromatic and a perfluoro-cyclohexadiene. The initial diene product is a specific isomer. This provides clean high-yield syntheses for those dienes and provides insight into the reaction mechanisms.

Results and Discussion

Composition of the Salts and Structural and Magnetic Properties. The high ionization potential of C_6F_6 ($\sim 10\text{eV}$)¹⁴ requires anions of very high ionization potential to stabilize the C_6F_6^+ cation in a salt. Clearly both PtF_6 (as shown earlier by Jha¹²) and IrF_6 (as shown in this study) bring about salt formation. If these salts have the composition $\text{C}_6\text{F}_6^+\text{MF}_6^-$ (which is probable), the lattice

energies would be¹⁵ approximately $-115 \text{ kcal mole}^{-1}$. The electron affinities of IrF_6 and PtF_6 have been determined^{16,17} to be 160 and 184 kcal mole^{-1} respectively, which means that the enthalpy of formation from the gaseous reactants:

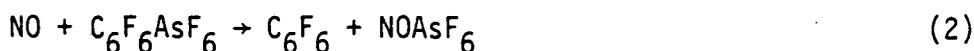


should be -45 and $-69 \text{ kcal mole}^{-1}$ respectively for the IrF_6^- and PtF_6^- salts. These anticipated reaction enthalpies are greatly in excess of those required to offset the unfavorable entropy change¹⁸ associated with (1). The inability of OsF_6 or the less powerfully oxidizing hexafluorides to form $\text{C}_6\text{F}_6\text{MF}_6$ salts is a consequence of their lower electron affinities ($\leq 130 \text{ kcal mole}$, see below). The instability of $\text{C}_6\text{F}_6\text{MF}_6$ ($\text{M} = \text{Ir}, \text{Pt}$) appears to be due to the relative ease of transfer of F^- from the anion to the cation in such instances (see below). Indeed this is a general problem in the stabilization of cations of the monocyclic perfluoro cations and the AsF_6^- , SbF_6^- and $\text{Sb}_2\text{F}_{11}^-$ anions appear to provide the best kinetic stability for such salts.

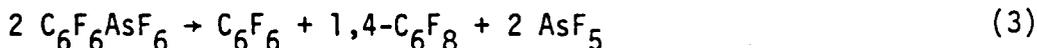
The first effective synthesis¹¹ of $\text{C}_6\text{F}_6\text{AsF}_6$ employed O_2AsF_6 as the oxidizer of C_6F_6 dissolved in liquid WF_6 . This solvent not only provided the desirable diluent effect for this hot reaction but its relatively high heat capacity also aided in preservation of a lower temperature. These are essential requirements for high yield syntheses of $\text{C}_6\text{F}_6\text{AsF}_6$ and its monocyclic relatives, since all are thermally unstable at ordinary temperatures. In more recent work sulfur chloride fluoride has been used as the diluent and moderator and the low working temperatures have resulted in greatly improved yields. Nevertheless, even with SO_2ClF , pyrolysis products from the salts are always observed

and a quantitative yield has never been obtained for any of the monocyclic cation salts. For these and other reasons¹⁹ the salt composition in each case has been determined from the stoichiometry of the salt pyrolysis products and other reaction stoichiometries.

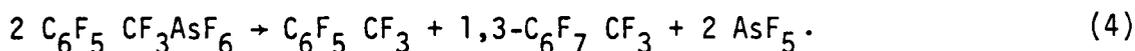
The spontaneous interaction of nitric oxide with $C_6F_6AsF_6$ is in harmony²⁰ with the ionization potentials ($I(NO) = 213$, $I(C_6F_6) = 230$ kcal mole⁻¹) and lattice energies¹⁵ ($C_6F_6AsF_6 = -115$, $NOAsF_6 = -130$ kcal mole⁻¹).



When this reaction is carried out by admitting nitric oxide very slowly to the $C_6F_6AsF_6$, the thermal decomposition products are present only in traces. Then the yield of $NOAsF_6$ is almost quantitative on the basis of the salt formulation $C_6F_6AsF_6$. This salt stoichiometry is also indicated by the ¹⁹F nmr spectra of the pyrolysis products. The spectra show C_6F_6 and 1,4- C_6F_8 to be present in 1:1 stoichiometry consistent with the reaction:

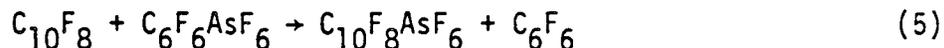


The product distribution in the decomposition of the perfluorotoluene cation salt similarly indicates that the stoichiometries are as follows:



With extension of the π systems from one ring to two there is a large decrease in ionization potential¹⁴ ($I, C_{10}F_8 = 204$ kcal mole⁻¹) and as the system becomes more extended the ionization enthalpy approaches that of graphite.

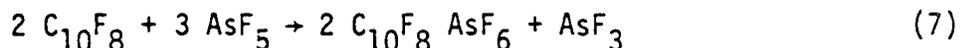
But the lattice energy of salts of all of these cations must depend primarily upon the closest approach of cation and anion, and since all of the cations have essentially the same thickness (that of the van der Waals distance²¹ between nearest-neighbor rings, which is $\sim 3.3\text{\AA}$), the lattice energy probably does not decrease as much as the greater size of the more extended cations would suggest. By comparison with C_6F_6 and $\text{C}_6\text{F}_5\text{CF}_3$ therefore, the electron oxidation of C_{10}F_8 and polycyclic aromatic relatives²² is comparatively easy. Not surprisingly then, $\text{C}_{10}\text{F}_8\text{AsF}_6$ can be prepared from the $\text{C}_6\text{F}_6\text{AsF}_6$ salt:



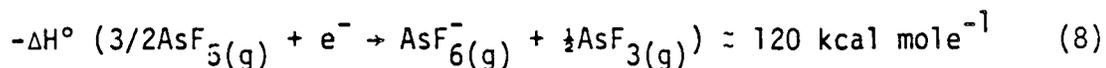
Since the thermal decomposition products of $\text{C}_6\text{F}_6\text{AsF}_6$ are all volatile whereas the $\text{C}_{10}\text{F}_8\text{AsF}_6$ is thermally stable and involatile at room temperature, a quantitative conversion of C_{10}F_8 to the salt can be achieved. This has settled the composition as $\text{C}_{10}\text{F}_8\text{AsF}_6$. It is not, however, necessary to employ $\text{C}_6\text{F}_6\text{AsF}_6$ as the oxidizer. A convenient, clean synthesis uses a mixture of AsF_5 and F_2 in SO_2ClF :



Perfluoronaphthalene is also oxidized by AsF_5 alone according to the equation:



This reagent is unable to oxidize the monocyclic perfluoro-aromatics because the electron affinity²³



is too low. Nor, for similar reasons, will the hexafluorides of tungsten ($E = 81 \text{ kcal mole}^{-1}$)²⁴ rhenium ($E = 106 \text{ kcal mole}^{-1}$)²⁵ or osmium ($E = 130 \text{ kcal mole}^{-1}$)²⁵ oxidize the single-ring perfluoroaromatics. In the case of $C_{10}F_8$, however, ReF_6 rapidly and quantitatively oxidizes it:



although WF_6 is unable to do so. It is therefore probable that AsF_5 or ReF_6 , although not particularly powerful oxidizers, will generate radical-cation salts from any of the multi-ring perfluoro (or perhydro) aromatics.

Although the crystal structure of $C_6F_6AsF_6$ has not been defined with satisfactory precision because of the degradation of single crystals in the X-ray beam (even at 143K), the structure has a rhombohedral unit cell containing one formula unit, $C_6F_6AsF_6$. The probable space group is $R\bar{3}$ and the site symmetry for each ion is D_{3d} . Indeed the cation could be essentially of D_{6h} symmetry in this lattice but the anticipated Jahn-Teller distortion should generate D_{2h} symmetry. The latter distortion could be present and masked by a random placement of the distorted species in the cation sites. The structural arrangement is one of cesium chloride type with each ion surrounded by a rhombically distorted cube of ions of the other kind. Unfortunately Raman spectra were not obtained for the $C_6F_6AsF_6$ salt and the infrared spectra are confused by the presence of

pyrolysis products. The infrared spectra do indicate AsF_6^- (ν_3 and ν_4 are observed) and fit a slightly modified C_6F_6 behavior consistent with the cationic formulation. Others have observed²⁶ a Jahn-Teller distortion in C_6F_6^+ but there is nothing to indicate that such a distortion is present in crystalline $\text{C}_6\text{F}_6\text{AsF}_6$.

The thermal stability of $\text{C}_6\text{F}_5\text{CF}_3\text{AsF}_6$ is even lower than that of the perfluorobenzene relative and because of this it is even less well characterized structurally, but the similarity of the g value from the e.s.r. spectrum, to that of $\text{C}_6\text{F}_6\text{AsF}_6$, points to the magnetic behavior being similar to that salt. The g value for the broad unresolved resonance observed for crystalline $\text{C}_6\text{F}_6\text{AsF}_6$ was centered at 2.0063. A septet similar to that reported earlier by Bazhin *et al.*² for C_6F_6^+ in superacid solutions was observed for a dilute solution of C_6F_6^+ $\text{Sb}_2\text{F}_{11}^-$ in SbF_5 at 77 K with a $g = 2.003$ also in agreement with the value given by the earlier workers. These free electron-like g values are in harmony with the simple Curie-Law paramagnetism observed for $\text{C}_6\text{F}_6\text{AsF}_6$. Although the presence of thermal decomposition products in the samples prevented reliable determination of the magnetic moment, the susceptibility dependence upon temperature followed the simple Curie Law. This shows that the radical cations, which are well separated and screened from one another in the $\text{C}_6\text{F}_6\text{AsF}_6$ lattice, are not interacting measurably at 4 K. The same Curie Law behavior is also observed in $\text{C}_{10}\text{F}_8\text{AsF}_6$, where the magnetic interactions between the cations must again be negligible.

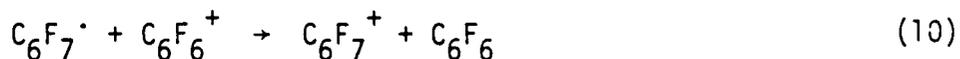
Even though $C_{10}F_8AsF_6$ is readily soluble in anhydrous HF and other solvents, all efforts to grow single crystals have failed. The X-ray powder data, however, were indexed and indicate a tetragonal unit cell (see EXPERIMENTAL). The dimensions of this cell suggest that the cations are aligned with their long axes parallel to the long axis of the unit cell, two such molecules being related by a 4_2 screw axis parallel to the long axis. The exact arrangement of cations and anions is not known but packing and symmetry considerations indicate that the anions must be symmetrically placed between facing cations and the cations thus screened well from one another, in accord with the observed simple paramagnetism.

In none of the $C_{10}F_8^+$ salt syntheses was there any indication of the existence of a polymeric-cation salt analogous to the $(C_{10}H_8)_2^+ PF_6^-$ salt described by Fritz and his coworkers²⁷. Face-to-face bonding of $C_{10}F_8$ with $C_{10}F_8^+$ appears not to be energetically favorable. This may be a consequence of the repulsive interaction of the electron-rich F ligands (particularly because of those electrons occupying the orbitals²⁸ of carbon-fluorine π -bonding character). The failure of the partially occupied π orbitals of the perfluoroaromatic cations to provide for effective bonding of the cations to one another has great impact on the physical properties of the salts. Thus the perfluoro-cation salts are electrical insulators (and simple paramagnets) whereas perhydropolycyclic relatives,²² and such salts²⁷ as $(C_{10}H_8)_2^+ PF_6^-$, are metallic.

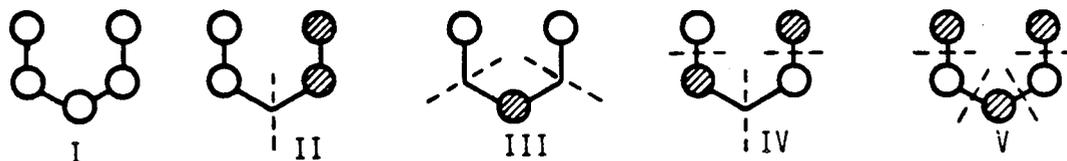
Relationship of Thermal Degradation to F⁻ Attack Products. That the interaction of the radical cations with nucleophiles has the potential of providing a special derivative chemistry is indicated by the products of F⁻ attack found in this work. One specific diene is obtained in quantitative yield in each instance. The thermal degradation of the salts yields the same fluorocarbon products as the F⁻ attack, indicating that the first step of the pyrolysis involves F⁻ transfer from anion to cation.

The interaction of F⁻ with the radical cation Ar⁺ (see Figure 1) involves²⁹ interaction of the HOMO of the F⁻ with the SOMO of the cation and electron transfer from the former to the latter. The subsequent step is equivalent to the interaction of F[•] radical with the aromatic molecule Ar. In this the interaction is strongest at the atom of Ar which makes the largest contribution to the LUMO. This initiates formation and location of the new C - F bond.

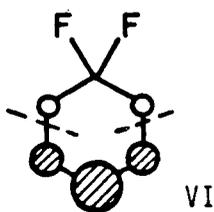
The ¹⁹F nmr spectra of the reaction products from the attack on C₆F₆AsF₆ by F⁻ show that the fluorocarbon products are C₆F₆ and the 1,4-diene in 1:1 molar ratio. These products are exactly the same as in the pyrolysis of the salt. The production of equimolar quantities of C₆F₆ and the diene C₆F₈ in both of these reactions is in harmony with rapid transfer of an electron from the addition product radical, C₆F₇[•], to another C₆F₆⁺ ion³⁰:



The nature of the diene formed in the interaction of a second F^- with the $C_6F_7^+$ is determined by the LUMO of the latter. The π system of the cyclohexadienyl cation is essentially that of a pentadienyl entity. The π orbitals of an idealized pentadienyl system, simply represented, are:



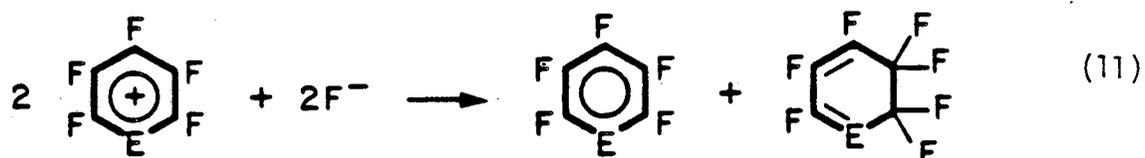
In the cation, the non-bonding orbital (III) is the LUMO. However, the situation is a little more complex in the case of $C_6F_7^+$ because of the high electronegativity of the carbon atom of the CF_2 group which causes the nodes to be swung towards the electronegative center. This amounts to a mixing of I and III and the LUMO has the form VI.



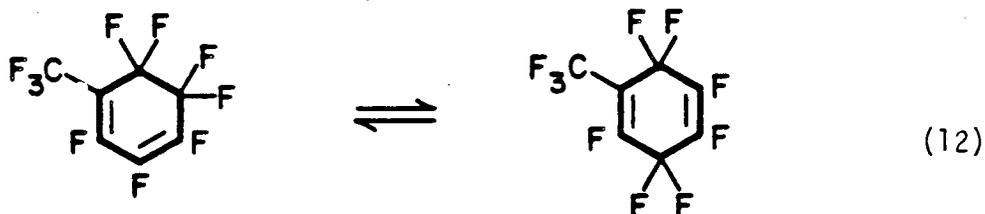
Thus the interaction of F^- with the $C_6F_7^+$ is strongest at the carbon atom para to the CF_2 group. This accounts for the 1,4-diene product.

In the case of the perfluorotoluene-cation salts, both F^- attack and pyrolysis again yield half a mole of the parent fluoroaromatic molecule and half a mole of diene. But now the diene is wholly the 1,3-

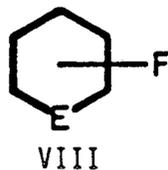
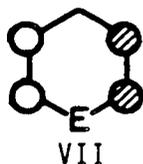
diene. These findings are essentially the same as those for the perfluoropyridine radical-cation salts,¹³ where F^- attack and pyrolysis produce half a mole each of C_5NF_5 and 1,3- C_5NF_7 . With representation of the more electronegative centers (C- CF_3 and N) by E, the interaction is:



That there must be strict electronic control of the reaction course which leads to the 1,3-diene is indicated by the observation that the diene subsequently isomerises in the toluene case³¹ to a 1:1 mixture of 1,3- and 1,4-dienes:



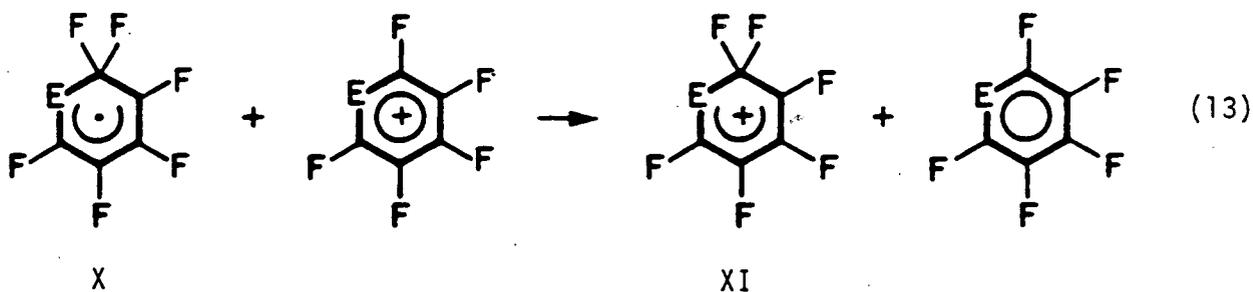
Unlike the $C_6F_6^+$ case, the site of F^- attack at the cation $C_5EF_5^+$ is crucial to the determination of which diene can subsequently form. The SOMO of $C_5EF_5^+$ has the form VII:



and this means²⁹ that the early transition state has F^- adding to $C_5EF_5^+$ as in VIII. The subsequent electron transfer from F^- HOMO to $C_5EF_5^+$ SOMO is followed by F^- orbital interaction with the C_5EF_5 LUMO. The latter has the form IX:

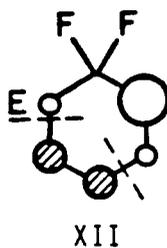


Since the node in SOMO VII determines the early-transition state geometry VIII, the F^- orbital (now SOMO) interaction with IX is determined by the large coefficients for the atoms ortho to E. This leads to radical X. This radical must lose an electron to another $C_5EF_5^+$:



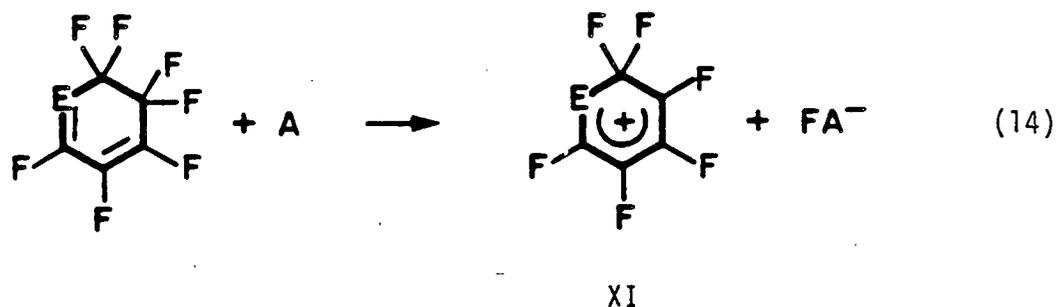
The nature of the $C_5EF_6^+$ LUMO of XI determines the site of the subsequent F^- attachment. That LUMO differs markedly from VI.

Because of the high electronegativity and excellent π -bonding character of the ring atom at E the nodes of the LUMO are swung towards E relative to their situation in (VI) and the LUMO has the form XII (the coefficients are exaggerated to clearly illustrate the effect of the nodal planes displacement).

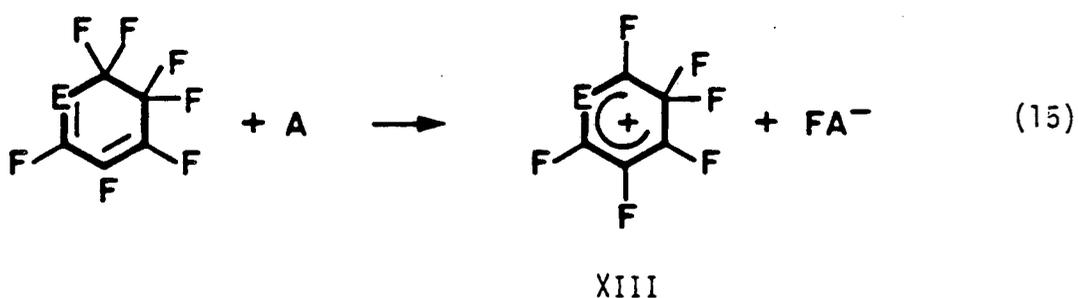


The preference for F^- attachment at the site ortho to CF_2 and meta to E accounts for the formation of the 1,3-diene.

Since the isomerization of the 1,3-to the 1,4-diene represented by equation 12 leads to an approximately 1:1 mixture, these isomers must be of comparable thermodynamic stability. It appears that the isomerization requires the presence of a fluoro acid, A (AsF_5 was present in twofold molar excess of the original 1,3-diene), hence it is likely that the first step in the isomerization involves F^- abstraction. Formation of cation XI:

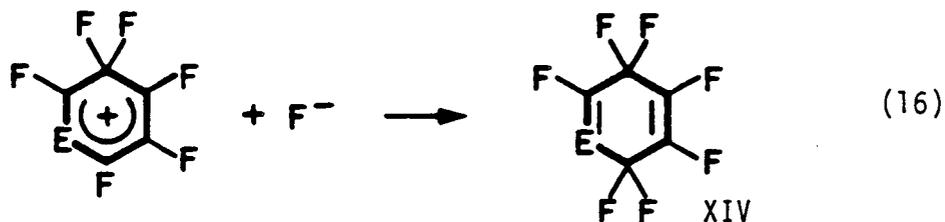


should lead to re-formation of the 1,3-diene for the reasons previously given. On the other hand, abstraction of F^- to generate cation XIII:

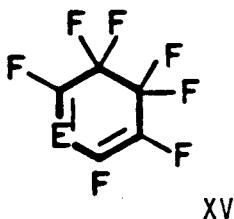


provides a new pentadienyl system. Since E is at the node of the idealized LUMO III, its influence is minimal and the LUMO of XIII closely resembles the $C_6F_7^+$ LUMO, VI. Therefore F^- attachment at cation XIII should occur preferentially

at the site para to the CF_2 group, thus providing for the observed 1,4-diene:



Of course F^- abstraction from the 1,4-diene XIV at the CF_2 ortho to E merely provides for repetition of the process in equation 16. In the case of F^- abstraction from the 1,4-diene XIV at the CF_2 meta to E, cation XI is formed and this again gives rise to the original 1,3-diene. Thus by F^- abstraction from each of the dienes, followed by F^- addition, each of the two observed dienes would be generated. These mechanisms, without other rearrangements in the intermediates, do not provide for the formation of the other possible 1,3-diene XV. It is not observed as a reaction product from



the C_5EF_5^+ salts and its synthesis via radical-cation salts appears to be ruled out.

The thermal decomposition of the monocyclic-cation salts must occur as a consequence of F^- transfer from anion to cation. Clearly, for the highest thermal stability, the best fluoride ion acceptors must be employed. These are SbF_5 (for SbF_6^- , $\text{Sb}_2\text{F}_{11}^-$ and $\text{Sb}_3\text{F}_{16}^-$ salts) and AsF_5 (for AsF_6^- salts).

Experimental Section

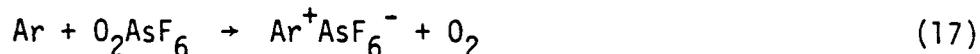
All manipulations were carried out in Kel-F, Teflon FEP, or fused silica reaction vessels attached to a stainless steel or Monel fluorine-type vacuum system and/or in a Vacuum Atmospheres inert atmosphere Dri-lab. Hexafluorobenzene, octafluorotoluene, octafluoronaphthalene (PCR Inc., Gainesville, FL), sulfur dioxide, anhydrous hydrogen fluoride (Matheson, E. Rutherford, NJ), cesium fluoride (ROC/RIC, Sun Valley, CA), trifluoroacetic acid (Aldrich, Milwaukee, WI), tungsten hexafluoride, arsenic pentafluoride and antimony pentafluoride (Ozark-Mahoning, Inc., Tulsa, OK) were used as received after checking their purity by infrared spectroscopy. Dioxygenyl salts³² and rhenium³³ and iridium³⁴ hexafluorides were prepared by literature methods. Sulfuryl chloride fluoride (Ozark-Mahoning) was distilled from O_2AsF_6 before use to convert the SO_2Cl_2 impurity to SO_2ClF , with elimination of Cl_2 .

Infrared spectra were obtained using Perkin-Elmer 337 and 597 infrared spectrophotometers. Raman spectra were recorded using a J-Y Ramanor HG-2S double monochromator in conjunction with Spectra-Physics 165 Kr-ion and Coherent Radiation Ar-ion lasers. ^{19}F nmr spectra were recorded using a Varian Associates NV-14 nmr spectrometer. Debye-Scherrer X-ray powder photographs of samples contained in dry thin-walled quartz capillaries (Charles Supper Co.) were obtained using a General Electric Powder Camera utilizing Ni-filtered Cu radiation. Precession photographs of single crystals of $C_6F_6AsF_6$ were taken using a Polaroid cassette on an Enraf-Nonius precession camera with Zr-filtered Mo radiation. Magnetic susceptibility measurements were carried out using a Princeton Applied Research vibrating sample magnetometer. Esr spectra were recorded using Varian Associates V4500 and E-3 spectrometers.

Syntheses of Perfluoroaromatic Radical Cation Salts:

Hexafluorobenzene Hexafluoroiridate(V). Hexafluorobenzene (2.6 mmol) dissolved in tungsten hexafluoride (2 ml) in a fused silica reactor to give a yellow-green solution. Iridium hexafluoride (2 mmol) was condensed into the reactor at 77K. At about 273K, the reaction mixture melted, and a bright orange solid rose to the surface of the WF_6 . The solvent and excess C_6F_6 were removed under vacuum at 298K. The dry orange solid decomposed rapidly, producing volatile carbon fluorides. Some of the iridium was reduced to the metal.

Hexafluorobenzene and Octafluorotoluene Hexafluoroarsenates(V). The bright yellow monocyclic cation hexafluoroarsenates were typically prepared (17)

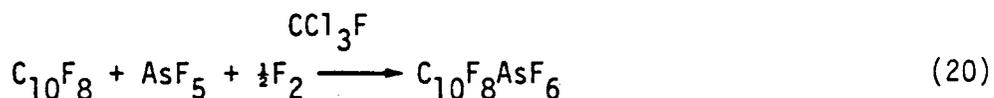
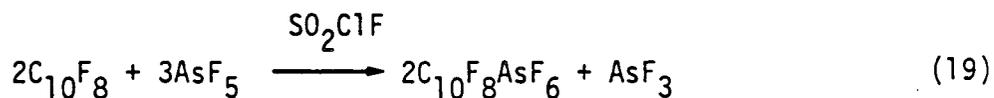
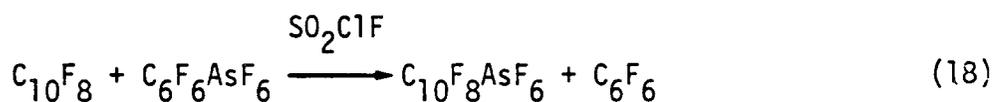


by co-condensing at 77K approximately 2 mmol of the aromatic species with 2 ml of either tungsten hexafluoride or sulfuryl chloride fluoride with 1.5 mmol of dioxygenyl hexafluoroarsenate in a pre-passivated fused silica reaction vessel equipped with a Whitey 1KS4-SS valve. The vessel was warmed slowly. The vigorous reaction, which ensued as soon as the solvent began to melt, was complete at 273K in WF_6 , or at 233K in SO_2ClF . Neither the dioxygenyl salt nor the product is soluble in either solvent; hence the product is a very fine powder. In order to ensure complete removal of unreacted reagents and volatile by-products (these were found to be minimized by the use of SO_2ClF) the reaction vessel was evacuated at 273K, then cooled to 195K for storage. Purification of the hexafluoro arsenates was achieved by rapid evacuation of the storage vessel at room temperature.

Hexafluorobenzene Fluoroantimonates. Fluoroantimonate salts, prepared in a similar manner from O_2SbF_6 and $O_2Sb_2F_{11}$ proved to be somewhat more thermally stable than the hexafluoroarsenates, although partial decomposition of the

former gave materials of mixed composition due to formation of bridged poly-anions $\text{Sb}_2\text{F}_{11}^-$ and $\text{Sb}_3\text{F}_{16}^-$ by reaction with SbF_5 formed in the thermal degradation reaction. Yields were generally about 60% but were strongly dependent upon the effectiveness of the heat dissipation; local heating caused decomposition of the product in each case.

Octafluoronaphthalene Hexafluoroarsenate(V). Emerald green $\text{C}_{10}\text{F}_8\text{AsF}_6$ (m.p. 395K) was prepared directly from O_2^+ salts (as above), by metathesis (18), from arsenic pentafluoride (19), or from a mixture of arsenic pentafluoride and elemental fluorine (20).



The last was found to be the most effective route to this octafluoronaphthalene salt, but is inapplicable to the syntheses of the monocyclic salts due to their relative instability at the temperatures required to maintain the starting materials in solution. $\text{C}_{10}\text{F}_8\text{AsF}_6$ was prepared in quantitative yield by metathesis: C_{10}F_8 (2.3 mmol) was added to $\text{C}_6\text{F}_6\text{AsF}_6$ (excess) in SO_2ClF . The reaction was complete in 30 minutes at 233K. Unreacted $\text{C}_6\text{F}_6\text{AsF}_6$ was decomposed at 298K, and the decomposition product pumped away, leaving pure $\text{C}_{10}\text{F}_8\text{AsF}_6$ (2.3 mmol).

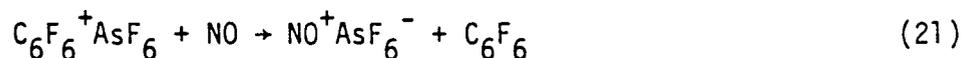
Octafluoronaphthalene Hexafluororhenate(V). Octafluoronaphthalene (0.42 mmol) was dissolved in dry trichlorofluoromethane (0.5 ml) at 273K in a fused silica

vessel. A slight excess of rhenium hexafluoride was admitted to the reaction vessel, causing the deep green octafluoronaphthalene hexafluororhenate(V) to precipitate at the vapor-liquid interface. The reaction was complete in less than one minute. The reaction vessel was evacuated at 295K to remove the solvent and unreacted rhenium hexafluoride, leaving the dry, free-flowing product, $C_{10}F_8ReF_6$ (0.42 mmol, 100% yield).

Solvents for Radical-Cation Salts. All of the perfluoroaromatic cation salts are readily soluble in anhydrous hydrogen fluoride, antimony and iodine pentafluorides, and in dry sulfur dioxide. The marked dependency of solubility in HF on temperature provided for the formation of crystals useful for single-crystal X-ray diffraction studies in the case of $C_6F_6AsF_6$. The freshly-prepared salt was dissolved in anhydrous HF at room temperature and the solution cooled slowly to 195K, when amber-colored needle-like crystals formed. Solvation by SO_2 prevented its use in growing single crystals of this and other radical-cation salts. Poorly crystalline materials were recovered from SbF_5 and IF_5 solutions perhaps because of the loss of solvent of crystallization from the first-formed crystals.

Reactions of Perfluoroaromatic Cation Salts.

Nitric Oxide. The reaction:



was always accompanied by some decomposition due to local heating. The controlled reduction of $C_6F_6^+$ salts with nitric oxide was, however, useful in establishing the stoichiometry of these materials. Freshly-prepared $C_6F_6AsF_6$ (0.66 mol) was exposed to dry NO gas in a fused silica reactor, producing $NOAsF_6$ (0.64 mol,

identified by its Raman spectrum and X-ray powder pattern) and C_6F_6 (0.68 mol, identified by nmr spectroscopy). The octafluorotoluene salt behaved similarly. $C_{10}F_8AsF_6$ did not react with NO.

Thermal Decomposition. $C_6F_6AsF_6$ decomposes smoothly at room temperature with a half-life of 15-20 minutes to arsenic pentafluoride and a colorless liquid, shown by infrared and ^{19}F nmr spectroscopy to be a 1:1 mixture of hexafluorobenzene and octafluoro-1,4-cyclohexadiene, C_6F_8 .³⁵

$C_6F_5CF_3AsF_6$ decomposes in a similar fashion to give arsenic pentafluoride and initially a 1:1 mixture of octafluorotoluene and 1,2,3,5,5,6,6-heptafluoro-4-(trifluoromethyl)-1,3-cyclohexadiene, $C_6F_7CF_3$ [nmr shifts³⁶ relative to internal CCl_3F : 58.8(3), 104.1(2), 113.5(2), 114.9(1), 153.2(1), 159.0(1)]. This 1,3-diene isomerized over a period of three days at room temperature in the presence of trifluoroacetic acid and AsF_5 to a 1:1 mixture of the 1,3-diene and 1,2,3,3,4,6,6-heptafluoro-5-(trifluoromethyl)-1,4 cyclohexadiene³⁷ [58.4(3), 110.0(1), 118.2(2), 125.9(2), 150.4(1), 152.1(1)].

$C_{10}F_8AsF_6$ is stable at room temperature, melting with slow decomposition at 395K. The products of thermal decomposition are arsenic pentafluoride, octafluoronaphthalene, and a complex residue containing traces of decafluoro-1,4-dihydronaphthalene, $C_{10}F_{10}$ (identified by its ^{19}F nmr spectrum).³⁸

Cesium Fluoride. Closely related to the thermal decomposition reactions are the interactions of the aromatic cation salts with cesium fluoride (see Discussion). $C_6F_6AsF_6$ in HF solution reacts rapidly with excess cesium fluoride, producing cesium hexafluoroarsenate and the 1:1 mixture of C_6F_6 and 1,4- C_6F_8 described above.

$C_{10}F_8AsF_6$ reacts more slowly with CsF, the green color of the radical cation persisting for up to one hour. The products found were the same as in the thermal decomposition.

Hydrolysis of $C_{10}F_8AsF_6$. Octafluoronaphthalene hexafluoroarsenate (1.1 mmol) reacted with excess water in the presence of CCl_4 (5 ml) to give a yellow solid. The ^{19}F nmr of this solid dissolved in methanol and benzene (1:1) showed it to be a 1:1 mixture of octafluoronaphthalene and hexafluoro-1,4-naphthalenedione, $C_{10}F_6O_2$.³⁹

Vibrational Spectra. Infrared spectra were obtained by pressing the freshly-prepared powders between silver chloride plates. In the case of $C_6F_6AsF_6$ products of thermal decomposition were present in each spectrum. By recording spectra at successive stages of decomposition, however, it was possible to distinguish those features due to the radical cation salt. In addition to the characteristic absorptions due to AsF_6^- , two strong bands appeared at 1490 cm^{-1} and 1030 cm^{-1} , which correspond to similarly strong absorptions at 1530 cm^{-1} and at 1019 and 994 cm^{-1} in neutral hexafluorobenzene. The infrared spectrum of $C_6F_5CF_3AsF_6$ was too complex to allow absorption due to the cation to be distinguished from those due to decomposition products. Intense fluorescence and thermal instability of the monocyclic cations prevented the recording of their Raman spectra even at very low temperatures. The Raman spectrum of $C_{10}F_8AsF_6$ was obtained by employing a Teflon rotating sample cell with a sapphire window. While the majority of vibrational modes in the cation are shifted only slightly in frequency from those in the neutral molecule, the relative intensities of some IR absorptions and Raman lines are greatly changed. In addition, the most intense feature in the

Raman spectrum of $C_{10}F_8AsF_6$ (the band at 420 cm^{-1}) has no observed counterpart in $C_{10}F_8$. The absence in the Raman spectrum of $\nu_1 AsF_6^-$ (which is ordinarily a strong band) hints at absorption enhancement of the cation Raman spectrum. On the whole, however, the overall framework of the molecule appears to be altered little by ionization. Moreover, the mutual exclusion of the IR and Raman activity appears to hold for the $C_{10}F_8^+$ ion (see Table I). Therefore it is likely that the cation is at least approximately centrosymmetric in its lattice site. It may retain the D_{2h} symmetry of the parent molecule.

Magnetic Susceptibility and ESR Spectra. The magnetic susceptibility of $C_6F_6AsF_6$ (Table II) obeys the Curie Law down to 3.8K. The low effective moment of 1.3 B.M. is probably due, at least in part, to decomposition of the pressure- and temperature-sensitive compound during manipulation to the degradation products which are diamagnetic. A higher moment was obtained for the more stable $C_{10}F_8AsF_6$, which also exhibits Curie Law behavior over the range 74 to 5.8K. For that salt μ (eff) = 1.68 B.M.

Esr spectra of dilute solutions of $C_6F_6Sb_2F_{11}$ in SbF_5 at 77K consist of a septet ($J = 20\text{ Hz}$) centered at $g = 2.003$, in agreement with results reported by Bazhin, *et al.*¹ for solutions of C_6F_6 in super-acid media. Esr spectra of $C_{10}F_8AsF_6$ in anhydrous HF or SbF_5 at 4K were unresolved, symmetrical resonances with $g = 2.004$.

X-Ray Diffraction. The Debye-Scherrer X-ray powder pattern of $C_6F_6AsF_6$ is given in Table III. Single crystals of $C_6F_6AsF_6$ were grown as described above. Due to thermal degradation and resultant fragmentation of these crystals, it proved impossible to collect sufficient high-quality diffractometer data for

a complete structure determination. Precession photographs did, however, establish the identity of the crystals and the bulk powder from which they were prepared. The data are consistent with a rhombohedral unit cell: $a = 6.60 \text{ \AA}(1)$, $\alpha = 106.0^\circ(1)$, $v = 246.1 \text{ \AA}^3$, $Z = 1$. Efforts to grow single crystals of $C_{10}F_8AsF_6$ were unsuccessful. The powder diffraction pattern, however, has been indexed (Table IV) on the basis of a tetragonal unit cell: (293K) $a_0 = 8.30(1)$, $c_0 = 18.76(1)$, $V = 1292 \text{ \AA}^3$; (213K) $a_0 = 8.26(1)$, $c_0 = 18.57(3)$, $V = 1267 \text{ \AA}^3$. Since AsF_6^- has an effective volume of $\sim 105 \text{ \AA}^3$ and the effective packing volume of $C_{10}F_8$ in its crystal⁴⁰ is 226 \AA^3 , the anticipated formula unit volume for the 1:1 salt is $\sim 330 \text{ \AA}^3$. The observed unit cell volume is therefore consistent with four formula units. Moreover, the dimensions of the unit cell indicate that the $C_{10}F_8^+$ species may be aligned with its long molecular axis⁴¹ ($\sim 9.6 \text{ \AA}$) parallel to \underline{c} . (The c_0 dimension is consistent with the molecules being arranged head to tail on a fourfold axis 4_2 .) The X-ray powder data for $C_{10}F_8ReF_6$ has not been fully indexed and is given in Table V. Similarity of the low angle d spacings with the data for $C_{10}F_8AsF_6$ suggests a close structural relationship but the salts are not isomorphous.

Acknowledgment.

The authors thank Professor J. C. Tatlow and Dr. R. Stephens of the University of Birmingham, U.K. for infrared spectra of the 1,3- and 1,4-C₆F₈ dienes which were helpful particularly in the early stages of this study. Professor R. Chambers and his coworkers, of the University of Durham, U.K. provided various samples of perfluoroaromatics essential to the research. Lessons in Frontier Orbital Theory, and detailed discussion of the course of the Ar⁺ + F⁻ interaction, were provided by our colleague Professor Andrew Streitwieser, Jr., to whom we are greatly indebted. One of us (N.B.) thanks the Warden and Fellows of All Souls College, Oxford, for the Visiting Fellowship, during the tenure of which this manuscript was first drafted. The work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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- (19) Fluoro-arsenates are notoriously difficult to analyse because of the kinetic stability of AsF_6^- , which persists even in aqueous solution in the presence of H_2S reagent. In addition the C-F bond is a very stable one and conventional combustion analysis cannot normally be applied to such fluorocarbon materials as these.
- (20) The entropy change for the reaction represented in equation (2) is approximately zero, but the enthalpy change could be less exothermic than indicated by these ionization potentials and lattice energies. The lattice energy given here for $\text{C}_6\text{F}_6\text{AsF}_6$ may have underestimated the dispersion energy contribution by as much as 5 kcal mole^{-1} bringing the $\text{C}_6\text{F}_6\text{AsF}_6$ lattice energy to a possible value of $\sim 120 \text{ kcal mole}^{-1}$.
- (21) The face to face contact between aromatic hydrocarbons such as that which occurs in the $(\text{C}_{10}\text{H}_8)_2\text{PF}_6$ structure (loc. cit.) of 3.2\AA and that in TCNQ complexes of 3.24\AA (Fritchie, C. J. Jr. Acta Cryst. 1966, 20, 892-898 and Kobayachi, H. Bull. Chem. Soc., Japan 1975, 48, 1373-1377) is comparable with the sheet to sheet separation in graphite of $\sim 3.3\text{\AA}$.
- (22) Coronene and other polycyclic hydrocarbons are electron-oxidized by $\text{C}_6\text{F}_6\text{AsF}_6$, and weaker oxidizers such as AsF_5 , to yield highly conducting salts (e.g. $\text{C}_{24}\text{H}_{12}^+\text{AsF}_6^-$). Richardson, T. J.; Tanzella, F. L.; Bartlett, N., to be published.
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- (25) On the basis of the electron oxidizing properties of the sequence of third transition series hexafluorides it has been argued (see Bartlett, N. Angewandte Chemie, Int. Ed. 1968, 7, 433-439) that the electron affinity increases approximately by 1eV (23.06 kcal mole⁻¹) for each unit increase in atomic number from WF₆ to PtF₆. With WF₆ (ref. 24) and PtF₆ (ref. 17) as fixed points, the increment becomes approximately 25 kcal mole⁻¹ and this yields E_a(ReF₆) ≈ 106 and E_a(OsF₆) ≈ 130 kcal mole⁻¹.
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- (28) Hexafluorobenzene has two sets of π orbitals: the lowest energy set (six orbitals) is primarily of C-F π -bonding character and is fully occupied; the higher energy set (six orbitals) are C-F π -antibonding but the occupied orbitals (three) also have ring π -bonding character (see Yim, M. B.; Wood, D. E. J. Am. Chem. Soc. 1976, 98, 2053-2057 and Brundle, C. R.; Robin, M. B.; Kuebler, N. A. J. Am. Chem. Soc. 1972, 94, 1466-1475. for evidence on the relative energies of the molecular orbitals).
- (29) We are indebted to Professor A. Streitwieser, Jr. for pointing out the details of the transition state for the Ar⁺ + F⁻ interaction, which are crucial to the understanding of the F⁻ addition ortho to E in the interaction with C₅EF₅⁺.

- (30) Arsenic pentafluoride is a strong fluoride-ion acceptor (ref. 15) with $\Delta H^\circ (\text{AsF}_5(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{AsF}_6^-(\text{g})) = -111 \pm 4 \text{ kcal mole}^{-1}$) whereas C_6F_7^+ must be a very weak acid. Hence the F^- transfer from AsF_6^- to C_6F_7 can be ruled out.
- (31) It may be that comparable isomerization of the 1,3 diene derived from the perfluoropyridine cation is prevented by the formation of a stable N-adduct with the AsF_5 .
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- (36) Integrated relative intensities in parentheses. Peak assignments and multiplicities are as follows: CF_3 (doublet of triplets), 5-F (multiplet), 60F (quartet), 3-F (multiplet), 2-F (septet), 1-F (multiplet). The composition C_7F_{10} is established by peak intensity integration. The large coupling constant J_{65} (22Hz) for the alicyclic (CF_2) groups confirms the 1,3-diene structure. Coupling is also observed between the trifluoromethyl group and 5-F but not 6-F, thus ruling out the 3- CF_3 isomer.
- (37) Integrated relative intensities in parentheses. Peak assignments and multiplicities are as follows: CF_3 (triplet), 4-F (multiplet), 6-F (multiplet), 3-F (triplet), 1-F (quartet), 2-F (triplet). This composition is also shown to be C_7F_{10} by peak integration. Here

no coupling is observed between the CF_2 groups. The similarity in the chemical shifts of the CF_3 groups in the two dienes indicates a similar CF_3 environment in each case.

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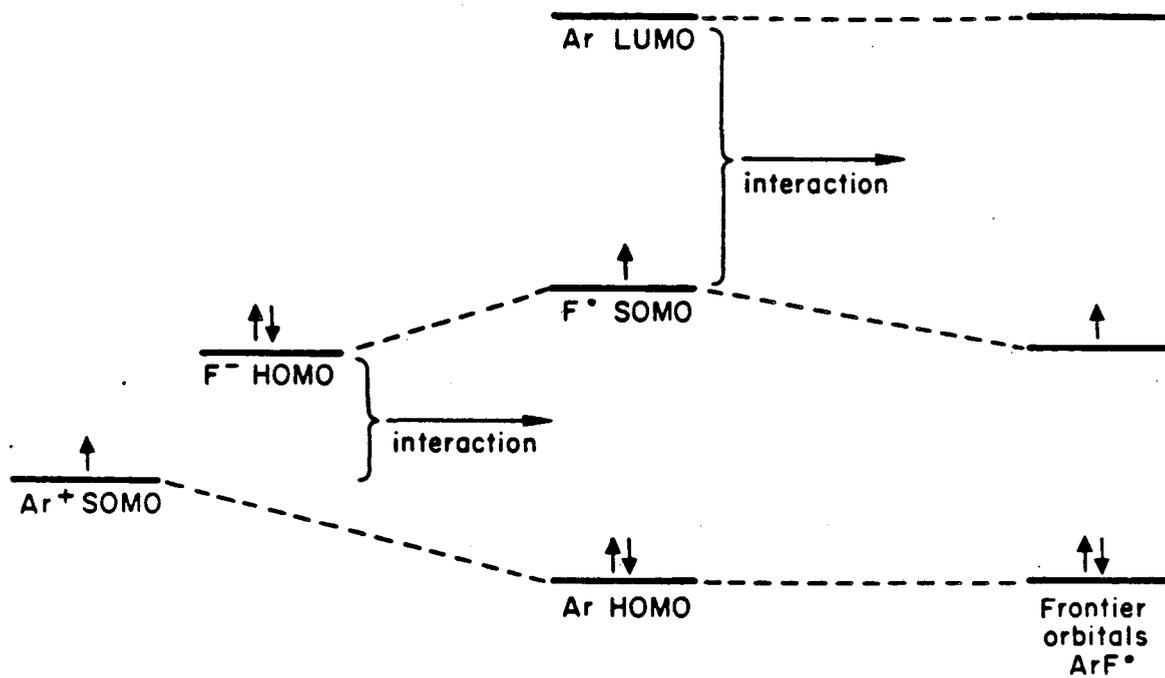


Figure 1. The Interaction of Ar^+ with F^-

Table I. Vibrational Frequencies of $C_{10}F_8^+$

Assignment ^a	$C_{10}F_8$ (Solid)		$C_{10}F_8^+$ in AsF_6^- Salt	
	IR	Raman	IR	Raman
		166 mw		164 w
				190 w
$\nu_{28}(b_{3g})$		291 m		284 w
$\nu_8(a_g)$		301 sh		
$\nu_{23}(b_{1u})$	317 w			
$\nu_{43}(b_{3g})$		339 mw		331 w
$\nu_{15}(b_{1g}), \nu_{27}(b_{2g})$		375 vs		382 m
$\nu_7(a_g)$		394 sh		396 m
$\nu_{34}(b_{2u})$	405 m			420 vvs
		432 vw	434 w	432 sh
$\nu_6(a_g)$		512 s		517 ms
$\nu_{42}(b_{3g})$		528 vw		540 w
$\nu_{22}(b_{1u})$	531 mw			
		577 vw		580 w
$\nu_{26}(b_{2g})$		601 mw		
		642 vw		646 s
$\nu_{45}(b_{3u})$	670 mw		675 w	
$\nu_{25}(b_{2g}), \nu_{41}(b_{3g})$		758 m		750 m
$\nu_{33}(b_{2u})$	784 s		790 s	784, 792 mw
$\nu_{21}(b_{1u})$	803 sh			
$\nu_{20}(b_{1u})$	946 s		940 vw	
	970 vw		977 s	
	1022 vw			
	1044 vw			

Table I. (Continued)

$\nu_5(a_g)$		1071 w		
$\nu_{40}(b_{3g})$		1083 vw		1097 mw
$\nu_{32}(b_{2u})$	1120 s		1118 vw	1122 m
	1145 vw		1135 w	
	1160 w		1170 s	
$\nu_{19}(b_{1u})$	1203 s	1198 w		
$\nu_4(a_g)$		1236 w	1245 s	
$\nu_3(a_g)$		1370 s	1380 s	1374 w
		1394 vw	1400 sh	1396 w
$\nu_{18}(b_{1u})$	1413 s		1415 w	1411 s
	1430 m		1450 sh	1451 m
$\nu_{30}(b_{2u})$	1480 s		1465 s	
	1547 w		1545 s	1556 m
			1580 s	
$\nu_1(a_g)$	1619,1624 m			1629 m
$\nu_{17}(b_{1u})$	1660 s		1690 m	
	1705 w		1725 w	

s = strong, m = medium, w = weak, sh = shoulder

^a Assignments after A. Girlando, B. Tamburini and C. Pecile, J. Chem. Soc. Faraday II, 1974, 70, 6.

Table II. Magnetic Susceptibility Data for $C_6F_6AsF_6$ and $C_{10}F_8AsF_6$

$C_6F_6AsF_6$	$C_6F_6AsF_6$
<u>T (K)</u>	<u>1/xm (cgs units)</u>
3.8	16.5
5.6	22.9
8.3	37.6
10.2	50.5
14.7	73.1
18.6	91.9
23.9	116.4
29.3	136.4
38.5	196.5
45.6	255.0
51.8	297.5
71.5	375.7

$C_{10}F_8AsF_6$	$C_{10}F_8AsF_6$
<u>T (K)</u>	<u>1/x m (cgs units)</u>
5.8	19.5
15.8	52.9
30.5	99.0
45.6	147.0
60.0	192.0
74.0	231.0

Table III. X-Ray Powder Data for $C_6F_6AsF_6$

Rhombohedral unit cell: $a_0 = 6.60(1)\text{\AA}$, $\alpha = 106.0(1)^\circ$, $V = 246.1\text{\AA}^3$, $Z = 1$,
 Probable Space Group $R\bar{3}$; Hexagonal Unit Cell: $a_0 = 10.55(1)$, $c_0 = 7.66(1)\text{\AA}$,
 $V = 738.4\text{\AA}^3$, $Z = 3$ (for observed reflections $-h + k + l = 3n$)

Hex. hkl	Rhomb. hkl	d_{hkl}	$10^4/d^2(\text{calc})$	$10^4/d^2(\text{obs})$	Relative Intensity
101	010	5.84	290	293	w
110	01 $\bar{1}$	5.29	359	357	vvs
021	11 $\bar{1}$	3.294	650	650	s
012	110	3.532	802	802	vs
211	02 $\bar{1}$	3.151	1009	1007	vs
300	$\bar{1}2\bar{1}$	3.054	1078	1072	vvw
202	020	2.948	1161	1151	vw
122,003	12 $\bar{1}$,111	2.550	1520,1534	1537	w
131	12 $\bar{2}$	2.408	1728	1725	w
113	120	2.308	1893	1877	vvw
312	03 $\bar{1}$	2.118	2239	2229	m
321	03 $\bar{2}$	2.021	2447	2448	w
303	030	1.955	2612	2615	w

Table IV. X-Ray Powder Data for $C_{10}F_8AsF_6$ (CuK_{α} , Ni Filter)(Tetragonal Unit Cells with: $(20^{\circ}) a_0 = 8.30(1)$, $c_0 = 18.76(1)$; $(-60^{\circ}) a = 8.26(1)$; $c_0 = 18.57(2)\text{\AA}$ Data for Sample at $\sim 20^{\circ}C$ Data for Sample at $-60^{\circ}C$

I/I_0	$\frac{1}{d^2} \times 10^4$		<u>hkl</u>	$\frac{1}{d^2} \times 10^4$	
	obs.	calc.		obs	calc
w	119	114	002	-	116
m	145	145	100	145	146.5
vw	159*				
m	176	173	101	176	176
vw	261	259	102	-	
vw	294	290	110	-	
m	323	318	111	322	322
vw	372*				
s	406	[401 [404	103 112	410	[408 [409
mw	460	454	004	465	464
w	502*				
s	552	546	113	559	554
vw	572	580	200	-	
s	613	608	201	617	615
vw	641*				
vs	699	694	202	712	702
vs	758	753	211	767	762
vw	798*				

Table IV. Continued

mw	844	[836 [836	203 212	858	[847 [849
vw	867	855	105	-	
vw	988	981	213	1008	995
vw	1021	1022	006		

* These lines are not indexable on the basis of a tetragonal cell and could be due to an impurity.

Table V. X-Ray Powder Data for $C_{10}F_8ReF_6$ (CuK_{α} Ni Filter) at 293K

I/I_0	$\frac{1}{d^2} \times 10^4$ (obs.)	(cont'd)	
vw	119	w	1760
vs	142	mw	1814
s	245	w	1922
w	276	w	1993
m	301	m	2128
s	394	m	2227
vw	440	w	2356
s	480	m	2475
s, br	583	w	2580
s	658	w	2678
vw	731	m	2765
s	792	m	2964
ms	832	w	3177
m	905	w	3387
m, br	1114	vw	3713
w	1221	vw	3801
w	1277	vw	4100
w	1324	w	4531
w	1359	vw	4815
w	1473	vw	5148
w	1530	vw	5853
vw	1657		

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