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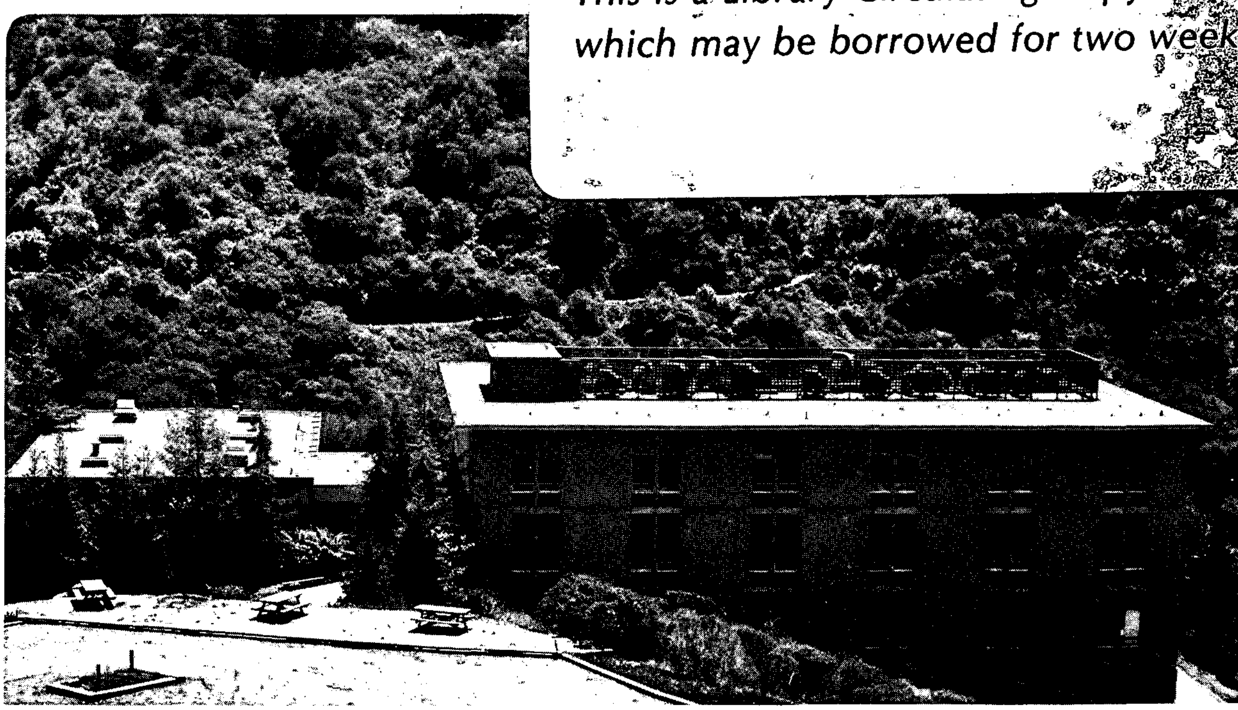

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COMPARISON OF PERFLUORO- AND PERHYDRO-POLYNUCLEAR AROMATIC HYDROCARBON CATION SALTS

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Abstract

Electron oxidation of the perfluoroaromatics C_6F_6 and $C_{10}F_8$ by O_2^+ salts yields salts of the radical cations $C_6F_6^+$ and $C_{10}F_8^+$ which are Curie-Law paramagnets. The perfluoro-analogs of the "metallic" $(C_{10}H_8)_2^+$ salts do not exist. Repulsive interactions involving the electron-rich fluorine ligands of the perfluoro-aromatics are probably responsible for the failure of these species to make metallic stacks. Attempts to prepare $C_6H_6^+$ salts have given the poly(paraphenylene) cation salts $(C_6H4)_n^+AsF_6^-$ which are good electronic conductors. Electron oxidation of perhydro-polynuclear aromatics by $C_6F_6^+$ salts or by AsF_5, e.g. $3AsF_5 + 2C_{24}H_{12} \rightarrow 2C_{24}H_{12}^+AsF_6^- + AsF_3$, yields what appear to be salts of the polynuclear aromatic cations. The magnetic and electrical properties of such salts are described.

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Introduction

Radical cation salts derived from hexafluorobenzene (1), octafluorotoluene (2), pentafluoropyridine (3) and octafluoronaphthalene (4) have been known for some time, and some of their reaction chemistry has been discussed in a recent publication.(5) Hexafluorobenzene hexafluoroarsenate, $C_6F_6^+AsF_6^-$, has oxidizing power sufficient to electron-oxidize most other mono- and polycyclic aromatics.

Fritz and co-workers (6) have prepared bis(naphthalene) salts, $(C_{10}H_8)_2^+MF_6^-$ (M = P, As) in which the aromatic molecules occur in stacks, resulting in metal-like electrical conductivity ($\sigma = 0.12 \pm 0.046\ \Omega^{-1}\ cm^{-1}$ for a polycrystalline pellet). This suggested the possibility of analogous behavior in the perfluoroaromatic series. Materials containing dimer cations, however, have not been isolated from reaction mixtures containing excess amounts of the neutral monomers, nor from controlled reduction of mono-cation salts. In each case, the cations are monomeric and magnetically independent of one another.

Attempts to prepare salts containing $C_6H_6^+$ have led to polymerization with HF-elimination, the resulting solid containing electron oxidized poly(paraphenylene).(7)

Thermally stable blue-green powders have been obtained by oxidation of coronene using O_2AsF_6, $C_6F_6AsF_6$ or AsF_5. Infrared spectra of these materials show the presence of the AsF_6^- ion in addition to the coronene-like cation. Gravimetry and elemental analyses indicate compositions ranging from $(C_{24}H_{12})_{4.0}AsF_6$ to

$(C_{24}H_{12})_{0.25}AsF_6$ with at least three crystallographically distinct phases indicated. In the X-ray powder diffraction patterns of these solids very strong reflections with d-spacings of about 3.3 suggest that the coronene species may be stacked in plate-like fashion. Crude resistance measurements on pellets of the polycrystalline powders indicate ambient-temperature conductivity for these salts in excess of $1.0 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$.

Experimental

The syntheses of cation salts of the monocyclic perfluoroaromatics and of octafluoronaphthalene have been described elsewhere.(1-5) Manipulations of air- or moisture-sensitive materials were carried out in a Vacuum Atmospheres Dri-Lab or in a stainless steel vacuum line fitted with Teflon FEP or fused silica reaction vessels.

The reaction of benzene with O_2AsF_6. In a typical reaction, benzene (0.403 g, 5.16 mmol) was co-condensed at 77K with sulfuryl chloride fluoride (8 ml) into a Teflon FEP reaction vessel containing O_2AsF_6 (0.912 g,4.13 mmol, prepared as in Ref. 8). On warming to 195K, a green solution was obtained from which oxygen evolved steadily for a period of fifteen minutes as the color faded. When the solvent and volatile products were removed at room temperature, a dark brown solid (0.893 g) remained. The product was washed with liquid anhydrous hydrogen fluoride to remove $(C_6H_5)_2AsF_2AsF_6$ formed by the reaction of benzene with AsF_5 present in the reaction mixture due to thermal decomposition of O_2AsF_6. The resulting brown powder (0.182 g) is diamagnetic, with room temperature conductivity (pressed pellet) in excess of $1.0 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$. Anal. [$(C_6H_4)_nAsF_6$, n = 4.06, based on C:As ratio], found: C,53.9; H,2.7; As,13.8; F,22.1%. $(C_6H_4)_{4.06}AsF_6$ requires: C,58.8; H,3.3; As,15.1; F,22.9%. The infrared spectrum (Figure 1) of the powder contains absorptions due to oxidized poly(paraphenylene) (10) and the hexafluoroarsenate(V) ion.

The reaction of benzene with $C_6F_6AsF_6$. $C_6F_6AsF_6$ was prepared *in situ* by reacting O_2AsF_6 (0.473 g, 2.14 mmol) with an excess of C_6F_6 in SO_2ClF prior to the addition of benzene (0.323 g, 4.14 mmol). The reaction was complete in one hour at 195K. The product (0.546 g, 0.134 g after washing with HF) was identical to that produced from O_2AsF_6. Elemental analyses of samples from four preparations gave values for n ranging from 1.8 to 4.4. The C:H ratio varied from 3.6 to 4.4 in eight analyzed samples.

The reaction of naphthalene with an excess of AsF_5. Naphthalene (0.20 g, 1.6 mmol) was dissolved in hexafluorobenzene (5 ml) in an evacuated Teflon FEP reactor. AsF_5 was admitted to the vessel at room temperature until a total pressure of 1 atm. was obtained. Copious amounts of a fluffy purple solid precipitated. Anal. C 59.78, H 2.81, C:H ratio 1.77. The solid was amorphous to x-rays.

In another experiment, a small amount of AsF_5 was added slowly to a solution of naphthalene in CH_2Cl_2 (mole ratio of AsF_5 to $C_{10}H_8$ ca. 1:6). Above the surface of the solution, where an excess of AsF_5 was present, the purple solid described above was formed. In the solution, however, a much darker, nearly black solid precipitated. Over a period of one to two hours following removal of the solvent, both products became grey. No x-ray pattern could be obtained from these solids.

Oxidation of coronene by O_2AsF_6. O_2AsF_6 (0.342g, 1.55 mmol) was placed in a Teflon FEP reaction vessel. A disc of Teflon filter paper was inserted above the solid, and coronene (0.464g, 1.55 mmol) was placed on the filter. Sufficient SO_2ClF was condensed into the vessel to cover the coronene. At 195K, the reaction proceeded slowly, reaching completion in one hour. The vessel was allowed to warm to room temperature, and volatile products were removed under vacuum after one hour. The product was a green, free-flowing powder. Anal. $[(C_{24}H_{12})_{0.97}AsF_6]$ C,H. The infrared spectrum of this solid (Figure 2b) contains, in addition to bands similar to those in neutral coronene, characteristic absorptions at ca. 700 and 400 cm^{-1} which are attributable to the v_3 and v_4 modes of hexafluoroarsenate (V). The magnetic susceptibility was found to follow the Curie-Weiss Law down to 12K with μ_{eff} = 0.36 B.M., Θ = -1.8°.

Oxidation of Coronene by excess $C_6F_6AsF_6$. $C_6F_6AsF_6$ was prepared in situ from O_2AsF_6 (1.0g, 4.5mmol) in SO_2ClF. The reaction vessel was held at 77K in a dry nitrogen-filled glove bag while coronene (0.15g, 0.50mmol) was added. The mixture was warmed to 195K, and the reaction allowed to proceed for 90 minutes. The product, obtained after removal of volatiles at room temperature was a dark-green friable powder. Anal. [$(C_{24}H_{12})_{0.5}AsF_6$], found: C,41.3; H,2.04%. $(C_{24}H_{12})_{0.5}AsF_6$ requires: C,43.3; H,1.82%. The infrared spectrum of this solid (Figure 2c) is similar to the more coronene-rich material described above, but the absorptions due to AsF_6^- are relatively more intense. The magnetic susceptibility exhibits Curie-Weiss behavior down to 6K with μ_{eff} = 0.83 B.M., Θ = -5.9°.

Oxidation of coronene by arsenic pentafluoride. Coronene reacted rapidly to give green and blue-green free-flowing powders on exposure to gaseous AsF_5 in a variety of solvents and at varying AsF_5 partial pressures. Solvents used included sulfuryl chloride fluoride, hexafluorobenzene, dichloromethane, trichlorofluoromethane and 1,1,1-trichlorotrifluoroethane. Arsenic trifluoride was detected as a reaction product by infrared spectroscopy. The color of the solid thus produced seems to be a qualitative measure of the extent of oxidation, the more highly oxidized materials being bluer than the coronene-rich solids. Product compositions were determined by gravimetry, with the assumption that arsenic is present only as AsF_6^- and that coronene is present as neutral molecules or electron-oxidized cations. Observed mole ratios of coronene to hexafluoroarsenate varied widely (4.0 to 0.25), smaller values being associated with the higher concentrations of arsenic pentafluoride. Debye-Scherrer photographs of the polycrystalline powders (Table I) show that the products differ significantly over the composition range and that neutral coronene, if present, is incorporated into the structures and not co-existing as a separate phase.

Results and Discussion

Chemical syntheses of radical cation salts by electron oxidation of neutral aromatic precursors require powerful oxidizing agents and stabilizing anions with high ionization energies (e.g. AsF_6^-, ReF_6^-, SbF_6^-, $Sb_2F_{11}^-$).(5) The stable salt of an aromatic cation of sufficient oxidizing strength can be employed as a synthetic reagent in the electron oxidation of other aromatics with lower ionization energies. Thus, hexafluorobenzene hexafluoroarsenate(V), $C_6F_6AsF_6$, provides a convenient one-electron oxidizing agent somewhat less energetic than the dioxygenyl salt ($I(O_2)$ = 281 kcal mol^{-1}; $I(C_6F_6)$ = 230 kcal mol^{-1}) (9) , from which it is most easily prepared:

$$O_2AsF_6 + C_6F_6 \rightarrow O_2 + C_6F_6AsF_6 \qquad (1)$$

The reduction product is the relatively inert and volatile hexafluorobenzene molecule. Moreover, the clean decomposition of $C_6F_6AsF_6$:

$$2C_6F_6AsF_6 \rightarrow C_6F_6 + 1,4\text{-}C_6F_8 + 2AsF_5 \qquad (2)$$

at room temperature to volatile products (5) means that an oxidation can be carried out using an excess of $C_6F_6AsF_6$. The remaining oxidant is then allowed to decompose in situ at room temperature and the volatile side-products are removed under vacuum. This technique has been applied in the quantitative preparation of octafluoronaphthalene hexafluoroarsenate ($I(C_{10}F_8) = 204$ kcal mol^{-1}):

$$C_6F_6AsF_6 + C_{10}F_8 \rightarrow C_6F_6 + C_{10}F_8AsF_6 \qquad (3)$$

In the two perfluoroaromatic cation salts, the cations appear to be well separated from one another by the anions. In $C_6F_6AsF_6$, each ion is surrounded by eight nearest neighbors of opposite charge in a distorted CsCl-type lattice. In the case of $C_{10}F_8AsF_6$, although details of the structure are not yet known, the symmetry and unit cell dimensions seem to preclude an arrangement involving stacks of overlapping cations.

Octafluoronaphthalene hexafluoroarsenate is exceptionally stable (dec. 395K), and in light of the report (6) of conductivity in $(C_{10}H_8)_2PF_6$, we sought to prepare the perfluoro-analog of this "synthetic metal". Repeated attempts using a variety of approaches have failed to produce such a material. Metallic behavior in partially-charged organic stacks derives from bonding interactions which occur as a consequence of overlapping of the HOMOs or SOMOs of the ring systems. This requires that the planar aromatic species be closer together than their van der Waals thickness of about 3.3 A, as has been observed in $(C_{10}H_8)_2PF_6$. Such a close juxtaposition of octafluoronaphthalene molecules, however would also bring the electron-rich F-ligands close together. This is probably a sufficiently strongly repulsive interaction to offset the weak bonding interaction between the electron-oxidized aromatic rings. Attempts to prepare a bis(hexafluorobenzene)$^+$ salt were also unsuccessful.

Although arsenic pentafluoride is able to electron oxidize:

$$3AsF_5 + 2e^- \rightarrow 2AsF_6^- + AsF_3 \tag{4}$$

its oxidizing power is weaker than that of $C_6F_6^+$. In the case of benzene, AsF_5 and C_6H_6 react quantitatively in HF or SO_2ClF (10) to give the colorless crystalline solid $(C_6H_5)_2AsF_2^+AsF_6^-$:

$$2C_6H_6 + 2AsF_5 \rightarrow (C_6H_5)_2AsF_2{}^AsF_6 + 2HF. \tag{5}$$

With O_2^+ or $C_6F_6^+$, however, benzene reacts to give poly-(paraphenylene) derivatives. While polymerization is never observed in the AsF_5 reaction, some of the diphenylarsonium salt is always formed in the O_2^+ and $C_6F_6^+$ reactions due to the presence in the reaction mixture of arsenic pentafluoride formed in the decomposition of the oxidizing agents. This suggests that the first step toward polymerization is electron oxidation of C_6H_6 (I = 212 kcal mol^{-1}) to $C_6H_6^+$, and that AsF_5 is not able to achieve this oxidation. Such an interpretation is consistent with the conclusions of other investigators as to the cationic nature of intermediates in the preparation of poly(paraphenylene).(11,12) As the number of fused or linked rings in a series of polynuclear aromatic molecules increases, the ionization energies of the neutral molecules decreases (I(biphenyl) = 183 kcal mol^{-1}, I(terphenyl) = 181 kcal mol^{-1}; I(naphthalene) = 187 kcal mol^{-1}, I(anthracene) = 171 kcal mol^{-1}, I(naphthacene) = 161 kcal mol^{-1}).

The polymer, which results when benzene is reacted with the powerful oxidizers O_2^+ and $C_6F_6^+$, is readily oxidized by AsF_5 (13,14) (which reagent, although not capable of initiating the polymerization of benzene, can polymerize the more easily oxidized phenylene oligomers, even including biphenyl).

While the perhydro-aromatics undergo hydrogen elimination readily upon oxidation (benzene(15) and naphthalene(16) can be polymerized electrochemically; binaphthyl is formed in the thermal decomposition of bis(naphthalene) hexafluorophosphate), the analogous elimination of F^+ in the perfluoro-aromatics is not energetically feasible.

For large, planar fused-ring systems, the tendency toward stacking of the multi-ring molecules in parallel array gives rise to behavior which is similar to that observed for graphite intercalation compounds. Coronene is rapidly oxidized by dioxygenyl hexafluoroarsenate, hexafluorobenzene hexafluoroarsenate, or arsenic pentafluoride:

$$nC_{24}H_{12} + O_2AsF_6 \rightarrow (C_{24}H_{12})_n{}^+AsF_6{}^- + O_2 \qquad (6)$$

$$nC_{24}H_{12} + C_6F_6AsF_6 \rightarrow (C_{24}H_{12})_n{}^+AsF_6{}^- + C_6F_6 \qquad (7)$$

$$2nC_{24}H_{12} + 3AsF_5 \rightarrow 2(C_{24}H_{12})_n^{+}AsF_6^{-} + AsF_3 \qquad (8)$$

The extent of oxidation and, thus, the observed stoichiometry, varies widely in the materials prepared by oxidation of coronene. The x-ray diffraction patterns of these solids are characteristic of the particular stoichiometries, but they have common features, the most striking being the presence in each pattern of a strong reflection with a d-spacing of about 3.3 A. This matches the thickness of a coronene molecule and suggests that these are stacked materials with the anions occupying interstices between the stacks.

H^+-elimination cannot be ruled out in the syntheses of the coronene derivatives described above, or for any of the other perhydro-aromatic systems in this study. Although the materials reported here appear to be homogeneous, containing arsenic only as AsF_6^-, the magnetic susceptibility data are not easily explained in terms of purely ionic formulations. The observed electrical conductivity may, therefore, be due either to stacking of the cations or to linking through HF elimination at the edges of the planar ring systems, or to a combination of the two. Clearly, the structures adopted by these materials are strongly influenced by the extent of oxidation and the sizes and number of anionic species present.

Conclusions

Electron-oxidation of perfluoroaromatic molecules produces mono-cationic salts whose thermal decomposition products are monomeric and result from disproportionation and auto-oxidation. The more strongly oxidizing salts, in particular $C_6F_6AsF_6$, can be used as synthetic reagents in the preparation of other radical cation salts. Whereas the perfluoro- cation salts contain single molecular cations with no apparent tendency for overlap of one cation with another, perhydroaromatic cation salts display a range of stoichiometries and structures in which cation-cation or cation-molecule interaction is favored. The perhydroaromatics also exhibit a tendency toward polymerization, resulting in chain polymers which are more readily oxidized than their monomer precursors to become electrical conductors.

Acknowledgements

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Table I. X-ray Powder Diffraction Data (d-spacings) for Coronene Salts: $(C_{24}H_{12})_nAsF_6$

n = 0.51

10.92w, 9.52m, 8.63vw, 7.57ms, 6.96s, 6.53s, 6.10w, 5.64w, 5.28s, 4.93m, 4.70m, 4.51vs, 4.44m, 3.98s, 3.52m, 3.33vs, 3.19w, 3.07vw, 2.78m

n = 0.89

12.42mw, 10.89w, 8.54m, 7.09vs, 6.49m, 6.08m, 5.43s, 5.14m, 4.79w, 4.58vvs, 4.36m, 4.17vw, 4.03m, 3.71vw, 3.54mw, 3.45mw, 3.35vs, 3.21s, 3.01w, 2.87w, 2.15w, 1.65w

n = 1.88

14.37w, 10.86ms, 7.54vs, 7.04m, 6.54vs, 5.31vs, 4.94vs, 4.67w, 4.35s, 4.19s, 4.02s, 3.72w, 3.61w, 3.50w, 3.32vvs, 3.16w, 2.33w, 1.66vw

n = 4.00

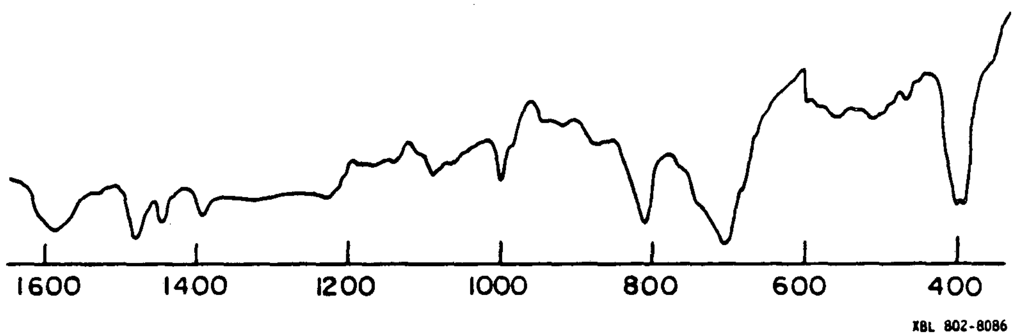
10.78w, 9.49s, 7.58vs, 6.47vs, 5.97vw, 5.25s, 5.11mw, 4.91w, 4.72w, 4.35s, 3.95s, 3.51s, 3.43m, 3.31vs, 3.20w, 3.16w, 3.06m, 2.77w, 2.66vw, 2.33m, 2.05vw, 1.96vw, 1.90w, 1.65vw, 1.47w

Figures

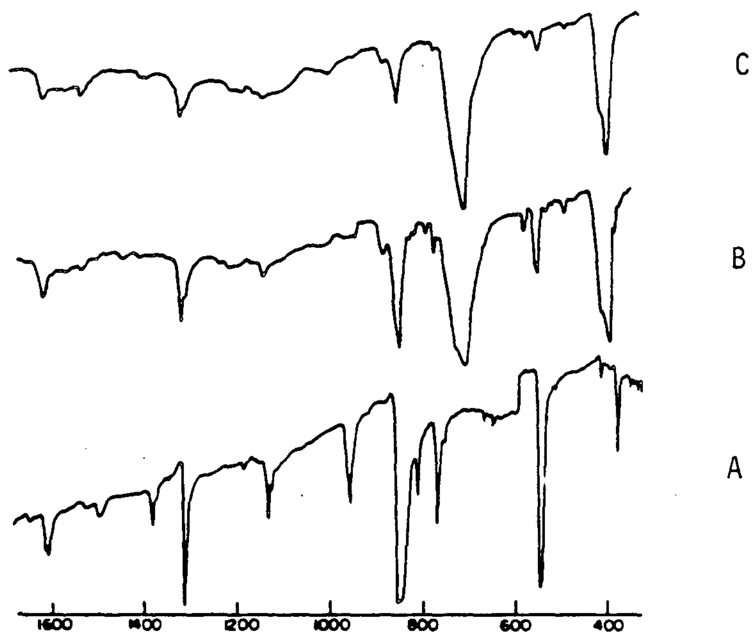
Figure 1. Infrared spectrum of oxidized poly(paraphenylene).

Figure 2. Infrared spectra of coronene and coronene salts.

INFRARED SPECTRUM OF OXIDIZED POLYPARAPHENYLENE



INFRARED SPECTRA OF CORONENE AND CORONENE SALTS



a) Coronene; b) $(C_{24}H_{12})_nAsF_6$: n = 0.97; c) $(C_{24}H_{12})_nAsF_6$: n = 0.51

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