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The Structure and Properties of Diethylfluoroalane, $(C_2H_5)_2AlF$[1]

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The unusually viscous compound diethylfluoroalane, $(C_2H_5)_2AlF$, has been characterized. Cryoscopic and ebullioscopic molecular weight determinations in benzene solution indicate the existence of a tetramer. Infrared, pmr, and F^{19} nmr spectra support a ring structure, with an alternating aluminum–fluorine backbone for the tetramer. The compound has acceptor properties weaker than those of the other dialkylhaloalanes. No stable ether adduct could be isolated, but the identity of amine adducts and their decomposition products has been established. Pyrolytic decomposition of $(C_2H_5)_2AlF$ yields ethane, in contrast to the olefins which have been reported for other alkylaluminum compounds. The high viscosity of liquid $(C_2H_5)_2AlF$ is believed to result from extensive Al–F–Al bridging to build polymeric frameworks.

Introduction

The alkylhaloalanes have been investigated extensively, with the exception of the fluoro compounds. Ziegler, *et al.*,[2] have prepared the first four members of the dialkylfluoroalane series and have pointed out the highly viscous nature of the dimethyl- and the diethyl-compounds. Jenkner[3] has disclosed a number of patents in which dialkylfluoroalanes are mentioned mainly as by-products, but details are lacking.

The viscous behavior of some of these fluoro compounds suggests association beyond the dimeric state characteristic of the other dialkylhaloalanes. Therefore we have undertaken a detailed study of a suitable example, $(C_2H_5)_2AlF$, in order to elucidate its structure and bonding.

Experimental Section

Synthesis of Diethylfluoroalane.—This compound was synthesized by the method developed by Ziegler,[3] using the reaction

$$(C_2H_5)_2AlCl + NaF \xrightarrow[\text{solvent}]{\text{xylene}} (C_2H_5)_2AlF + NaCl$$
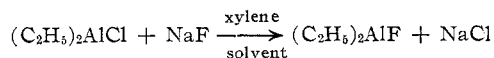
All operations were carried out in an atmosphere of very dry nitrogen because of the pyrophoric nature of the compounds. In a typical preparation, 0.685 mole of diethylchloroalane with a slightly more than equimolar amount of sodium fluoride was stirred vigorously in refluxing xylene. From time to time the course of the reaction was checked by allowing the suspended

(1) Presented in part at the Symposium on Inorganic Polymers, University of Western Ontario, London, Ontario, Sept 1963. Extracted from the thesis submitted by G. F. Lengnick in partial fulfillment of the requirements for the Ph.D. degree, June 1964, Cornell University.

(2) K. Ziegler and R. Köster, *Ann. Chem.*, **608**, 1 (1957); K. Ziegler, E. Holzkamp, R. Köster, and H. Lehmkuhl, *Angew. Chem.*, **67**, 213 (1955).

(3) H. Jenkner, German Patent 1,009,630 (1957), and others. See *Chem. Abstr.*, **53**, 21667b (1959).

material to settle and then analyzing the clear supernatant liquid for chlorine. The reaction was found to be complete after 12 hr. The xylene was then distilled from the reaction mixture at room temperature *in vacuo* at a pressure of not less than 10^{-2} mm. The residual liquid diethylfluoroalane was separated from the solids by distillation through a heated, spiral-packed fractionating column of 2.5-cm diameter and 20-cm length. The colorless, extremely viscous liquid distilled over at a head temperature of 55° (0.016 mm) [lit.[3] 90–91° (0.4 mm)] and a pot temperature of 145–200°. Frequent warming of the receiver inlet (at least 2-cm wide) was necessary to prevent plugging by the viscous diethylfluoroalane. A yield of 76% of pure compound was realized.

Storage and Handling.—The high viscosity and pyrophoric nature of diethylfluoroalane necessitated unconventional manipulative techniques. Samples were stored in small fragile Pyrex bulbs which were filled from the distillation receiver by gently heating the substance in an atmosphere of nitrogen, thus decreasing its viscosity markedly and permitting it to flow into the bulbs.

Transferring a weighed quantity of diethylfluoroalane was accomplished by its dissolution in a weighed amount of hydrocarbon solvent in the special apparatus shown in Figure 1. The weighed fragile glass bulb under nitrogen was crushed with the glass rod. Then the solvent was admitted in small portions from a syringe inserted through the serum cap on the side arm, dissolving the material and leaving the glass chips on the medium filter frit, where they were tared. It is not advisable to remove the solvent *in vacuo*, for its very slow removal is further complicated by the partial evaporation of diethylfluoroalane.

Diethylfluoroalane is compatible with Apiezon greases and deKhotinsky cement, but not with silicone grease. Upon exposure of the compound to air, the resulting oxidation reaction, generally accompanied by flame, causes etching of adjacent glass surfaces.

Analysis.—Diethylfluoroalane and derivatives, subsequently prepared, were hydrolyzed in an evacuated system at −78° by breaking a weighed crushable sample bulb with a magnetically operated plunger and then adding 2-propanol, followed by 1.0 N
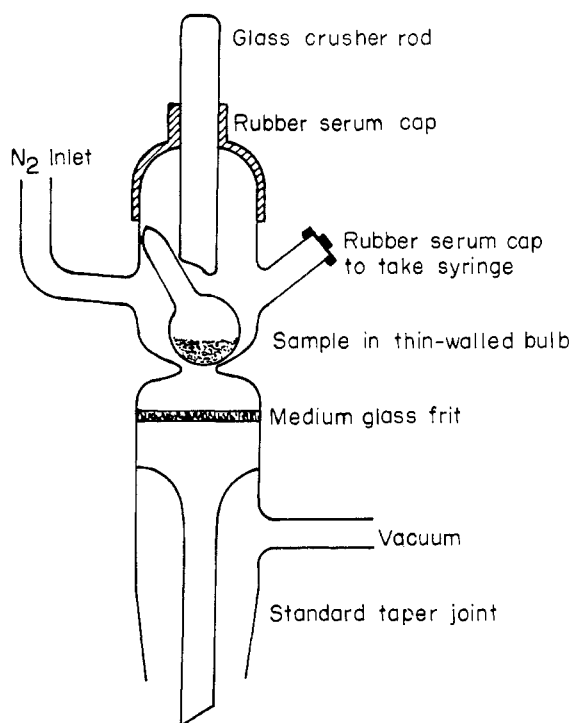
Figure 1.—Sample-transfer apparatus.

nitric acid in 2-propanol. Upon warming to room temperature ethane evolution was completed. The ethane was trapped and purified in a vacuum system and its quantity determined.

Aliquots of the residual nitric acid solution were analyzed for aluminum by precipitation with 2-hydroxyquinoline (oxine). Fluoride ion interferes strongly with the formation of the oxinate in acidic solution but complete precipitation was realized by using an ammoniacal solution, as adopted from a separation procedure due to Lundell and Knowles.[4]

Anal. Calcd for $(C_2H_5)_2AlF$: Al, 25.95; C_2H_5, 55.80. Found: Al, 26.05, 26.28; C_2H_5 (as C_2H_6), 55.63, 56.6.

Physical Properties.—Attempts to grow crystals of diethylfluoroalane from hydrocarbon solutions failed. However, sublimation of the substance onto a cold finger at $-196°$ produced a white frosty layer which changed irreversibly to a glassy appearance at $-128 \pm 5°$. The compound therefore does not have a true melting point but must suffer gross rearrangement during this phase transition.

The density of $(C_2H_5)_2AlF$ was determined using a pycnometer which could be attached to the vacuum system and filling it in the manner already described. The density was found to be 0.992 ± 0.003 g/cc at 24.1°.

Refractive index measurements were made by mounting a thermostated Abbé refractometer in a polyethylene glove bag to prevent exposure to air. Values obtained for $n^{25}D$ varied between 1.4169 and 1.4170.

Quantitative solubility data have not been determined, but diethylfluoroalane is readily soluble in aromatic, aliphatic, and alicyclic hydrocarbons and in ethyl ether.

Molecular Weight Determination.—Cryoscopic and ebullioscopic measurements were made in benzene solution. The solvent was purified by drying the AR grade over phosphorus(V) oxide, filtering, and fractionally distilling over potassium through a 3-ft packed column. A redistilled middle fraction melted at 5.30° (lit.[5] 5.325–5.335°).

The cryoscope was constructed so that it could be sealed and evacuated to permit measurements either *in vacuo* or under nitrogen. An electromagnet activated a wire stirrer. The sample was introduced by crushing a sample bulb in a side arm with a glass rod mounted vacuum-tight in a rubber serum cap.

A temperature reproducibility of 0.001° with a cooling rate of 0.1°/min was realized. Calibration with naphthalene compensated for solvent holdup, the presence of solvent in the vapor phase, etc. The molecular weight of diethylfluoroalane was found to be 422 ± 16 in a concentration range of 0.00508 to 0.0403 *m*. This compares to 416.4 calculated for the tetramer. There was no observable concentration dependence.

The ebullioscopic measurements were made in a Swietoslawski double-chamber differential ebullioscope[6] which was modified to operate under a nitrogen atmosphere at constant pressure. The sample was introduced by using the previously described sample-addition apparatus mounted on the ebullioscope. A weighed amount of solvent was used to wash the sample down. Calibration of the apparatus with diphenyl showed that the solvent volume could be varied between 20 and 30 ml without changing the boiling point elevation constant. Therefore the concentration could be varied by adding solvent in small increments. By this method the molecular weight of diethylfluoroalane was found to be 408 ± 10, which again indicates a distinct molecular tetramer species in solution. Concentration effects were not noticed in the observed range of 0.0618 to 0.0977 *m*.

Nuclear Magnetic Resonance Studies.—A Varian Associates Model A-60 nmr spectrometer was used to obtain the proton spectrum of pure diethylfluoroalane and of several hydrocarbon solutions thereof from room temperature to $-60°$. Sample tubes were filled by warming the viscous material to permit flow from a storage bulb. Solvent was then condensed on top of the sample to dissolve it. Chemical shifts of CH_3 and CH_2 protons with reference to the solvent were measured and are summarized in Table I. Area ratios of CH_3/CH_2 protons yielded an average of 1.61 by electronic integrator, and the coupling constant *J* at 8 cps was the same for all samples. The spectra are all alike, irrespective of solvent and temperature, as is indicated by the constant difference between the methyl and methylene proton shifts ($D = \Delta CH_3 - \Delta CH_2 = -61$ cps). This constancy and the absence of a new set of peaks at lower temperature is good evidence that the ethyl groups are all equivalent. If rapid exchange of dissimilar groups at room temperature had been taking place, this should have been arrested at $-60°$, giving rise to new peaks. Therefore all ethyl groups in diethylfluoroalane must be terminal and none can be bridging groups. That ethyl bridging can be detected in this manner has been shown by Groenewege, *et al.*,[7] who report two types of ethyl groups for the triethylalane dimer at lower temperatures. A noteworthy feature of the spectrum is the appearance of the CH_2 proton spectrum at higher magnetic field strength than that of the CH_3 protons. This is characteristic of many metal alkyls but seems especially well pronounced in this compound, probably due to the influence of the fluorine atoms.

TABLE I

PROTON CHEMICAL SHIFTS[a] OF DIETHYLFLUOROALANE

Sample	Temp, °C	ΔCH_3, cps	ΔCH_2, cps	D ($\Delta CH_3 - \Delta CH_2$), cps
Pure	25	...	...	−61
In benzene	25	355	418	−63
In cyclopentane	25	27	88	−61
In cyclopentane	−50	26	87	−61
In cyclopentane	−60	26	87	−61

[a] Chemical shifts are reported in reference to solvent peak.

Fluorine nmr spectra of a 25% cyclohexane solution of diethylfluoroalane were obtained[8] at 25° and at 0°. A 2-mm diameter sealed capillary filled with fluorobenzene served as external standard. This method of introducing the reference

(4) G. E. F. Lundell and H. B. Knowles, *Bur. Std. J. Res.*, **3**, 91 (1929).

(5) K. S. Pitzer and H. S. Gutowsky, *J. Am. Chem. Soc.*, **68**, 2204 (1946).

(6) W. Swietoslawski, "Ebulliometric Measurements," Reinhold Publishing Corp., New York, N. Y., 1945, p 10.

(7) M. P. Groenewege, J. Smidt, and H. de Vries, *J. Am. Chem. Soc.*, **82**, 4425 (1960).

(8) The assistance of Dr. W. M. Ritchie of the Standard Oil Company of Ohio in obtaining the fluorine nmr spectra is gratefully acknowledged.

TABLE II

COMPARISON OF INFRARED SPECTRA (CM⁻¹)

$(C_2H_5)_2AlF$	Intensity	$(C_2H_5)_2AlCl^a$	$(C_2H_5)_3Al^a$	Assignment
2877	s		Only pertinent	
2797	ms (sh)	Not given	peaks are listed	C–H str
2740	ms (sh)			
1468	ms	1470		CH₃ asym bend
1458	ms	1460		
1412	s	1410		CH₃–Al bend
Absent	s	Absent	1401	CH₂–Al bridge bend
Absent	s	Absent	1389	
1374		1380		CH₃ sym bend
1230 (1234)	ms	1230 (1234)		CH₂ tilt
Absent	s	Absent	1218	CH₂ bridge tilt
1203 (1211)	s	1200 (1205)		CH₂ twist
992 (996)	s	990 (996)		
956 (963)	s	955 (962)		C–C str
925 (930)	ms	925 (932)		
870–841	m			See discussion
823	m			
804–797	m			
697–672 (687)	s	673 (676)		Al–C mode
(615)	vs	628 (628)		CH₂ rock
Absent	s	544 (546)		Al–C in dimer
Absent	m	438 (435)		Al–X–Al in dimer

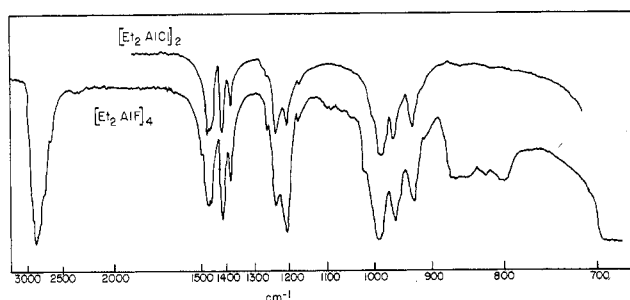*a* Spectra due to Hoffmann.[9] Numbers in parentheses are due to Mach.[11]

Figure 2.—Infrared spectra of $(C_2H_5)_2AlF$ and $(C_2H_5)_2AlCl$.

avoided its reaction with the sample. Only a singlet at 46.5 ± 1 ppm above fluorobenzene was observed, the spectra being alike at both temperatures. The absence of any kind of line broadening at 0° (below the freezing point of the solution) indicates the magnetic equivalence of the fluorine atoms in the molecule.
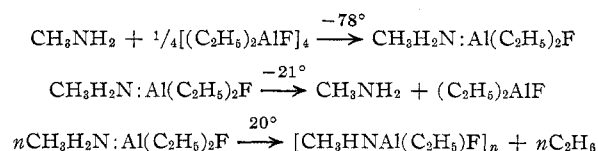
Infrared Spectrum.—A Perkin-Elmer Model 21 infrared spectrophotometer was used to obtain the absorption spectrum shown in Figure 2, the spectrum of $(C_2H_5)_2AlCl^9$ being superimposed for comparison. The cells were prepared in a drybox by smearing the pure substance directly on the windows and sealing the window edge with Apiezon grease to prevent oxidation. Table II lists frequencies and assignments and makes a comparison with the spectra of the diethylchloroalane and triethylalane dimers.[9] The most interesting feature of the spectrum, as far as the structure of diethylfluoroalane is concerned, is the total absence of frequencies due to bridge-ethyl motions. Hoffmann[9] has made detailed assignments to such modes for $[(C_2H_5)_3Al]_2$ (1401 and 1389 cm⁻¹ for the CH₂–Al bending mode, 1218 cm⁻¹ for the CH₂ tilting mode) and has shown that these vanish in $[(C_2H_5)_2AlCl]_2$, which he correctly assumes to be halogen-bridged. Our data then show that ethyl bridges, like those in triethylalane, are not responsible for the coordinating link between individual $(C_2H_5)_2AlF$ units. The broad bands between 797 and 870 cm⁻¹ cannot be assigned with certainty but may be compared to the Al–F frequencies reported[10] for NaAlF₄ (853–880 cm⁻¹) and LiAlF₄ (775–783 cm⁻¹) in the gas phase. Alter-

nately, these bands might conceivably originate in interactions with the NaCl window material, but this is very unlikely since the solution spectrum by Mach[11] does not clearly reveal them. Furthermore, the windows were not etched, and it is known that such interactions only occur at high temperatures.

Reaction with Ethyl Ether.—An excess of dry ethyl ether (22.68 mmoles) was added at −196° to 2.46 mmoles of diethylfluoroalane (based on monomer weight). Upon warming to −78° the metal alkyl dissolved in the ether, but the latter could be recovered almost quantitatively at this temperature at a pressure of 10⁻³ mm or less. Thus a stable ether adduct was not formed.

Reaction with Trimethylamine.—Trimethylamine (3.935 mmoles) was condensed onto 2.333 mmoles of diethylfluoroalane dissolved in 30.0 ml of pentane. The mixture was kept at −78° for 10 hr. A white crystalline precipitate formed. Excess amine (1.650 mmoles) was recovered at −78° *in vacuo*, leaving a compound with an experimental stoichiometric amine to alane ratio of 0.981:1. This 1:1 adduct melted at −20.5 to −18.5° and decomposed to the starting materials. The observed volatilization and ready vacuum transfer of the diethylfluoroalane produced in this dissociation are evidence for the existence of at least transient monomeric units of this compound in the vapor phase.

Reaction with Methylamine.—Excess CH_3NH_2 (9.13 mmoles) was condensed onto 8.09 mmoles of $(C_2H_5)_2AlF$ in 30.0 ml of pentane. White needles were observed at −78°. The excess amine (1.49 mmoles) and the solvent were removed at this temperature, leaving an adduct with an amine to alane ratio of 1:1.06. Upon warming to −21° dissociation of the adduct released methylamine slowly, but at temperatures approaching 20°, ethane evolved as the additional major component. Within 3 days at room temperature a hard glassy mass had formed. Analysis failed to establish accurate elemental stoichiometry for this material. It seems likely that the following reactions occurred.

$$CH_3NH_2 + \frac{1}{4}[(C_2H_5)_2AlF]_4 \xrightarrow{-78°} CH_3H_2N:Al(C_2H_5)_2F$$

$$CH_3H_2N:Al(C_2H_5)_2F \xrightarrow{-21°} CH_3NH_2 + (C_2H_5)_2AlF$$

$$nCH_3H_2N:Al(C_2H_5)_2F \xrightarrow{20°} [CH_3HNAl(C_2H_5)F]_n + nC_2H_6$$

(9) E. G. Hoffmann, *Z. Elektrochem.*, **64**, 616 (1960).

(10) L. D. McCory, R. C. Paule, and J. L. Margrave, *J. Phys. Chem.*, **67**, 1086 (1963).

(11) K. Mach, *Collection Czech. Chem. Commun.*, **28**, 2295 (1963).

The last two reactions may have occurred simultaneously yielding mixed and undefined products. Furthermore, possible additional condensation[12] of $[CH_3HNAl(C_2H_5)F]_n$ may make characterization of the final glassy product very difficult.

Pyrolysis of Diethylfluoroalane.—Noticeable decomposition was evident after 11.5 hr of heating at 298 ± 1.0° in a sealed tube, but 130 hr was necessary to totally degrade a 9.97-mmole sample. The volatile products were fractionated, weighed, and identified by infrared and mass spectrometry.

Fraction collected at °C	Principal constituent	Mole %
−196	C_2H_6	93.9
−96	C_4H_{10}	3.6
−78	C_6 hydrocarbons	2.5

The solid nonvolatile residue contained metallic aluminum (shown by X-ray diffraction) and an unidentified yellow solid. The most significant feature of the pyrolysis is the evolution of ethane, not only as a final product but also as the only volatile product of the initial decomposition step. (This was shown by pyrolysis in a mass spectrometer.) Such a pyrolysis pattern contrasts with that of triethylalane where ethylene is the major initial gaseous product resulting from the reaction[13]

$$(C_2H_5)_3Al \longrightarrow (C_2H_5)_2AlH + C_2H_4$$

One must conclude that the decomposition of diethylfluoroalane occurs mainly *via* a free radical mechanism and not *via* the olefin elimination mechanism which is operative in the pyrolysis of other organoalanes.

Discussion

The Structure of the Diethylfluoroalane Tetramer.— The molecular weight data in benzene have established the tetrameric nature of diethylfluoroalane. Neither concentration nor temperature appears to have a significant effect on the molecular weight, indicating the presence of strongly associated units and the predominance of a stable tetrameric molecular species.

This tetrameric molecule shows equivalence of ethyl groups at room temperature and below, a fact of great significance in the choice of a reasonable structural model. A chain structure, such as
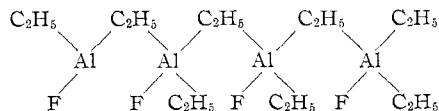
would have several types of ethyl groups, and even if their exchange is rapid, this structure must be excluded from the possibilities because the low-temperature nmr spectrum would have revealed their nonequivalence. The same can be said for a chain structure in which fluorine forms the bridging link, *i.e.*
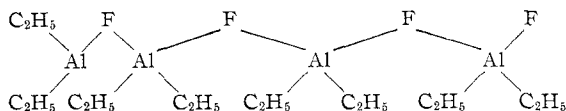
The fluorine nmr spectrum also eliminates both of the above structures which involve nonequivalence, whereas, experimentally, only equivalent fluorine
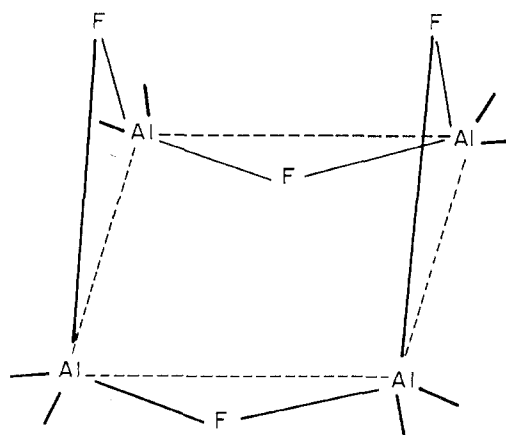
(12) A. W. Laubengayer, J. D. Smith, and G. G. Ehrlich, *J. Am. Chem. Soc.*, **83**, 542 (1961).

(13) Y. A. Tajima, F. Salser, and C. J. Marsel, "The Thermal Decomposition of Aluminum Triethyl," Research Division, College of Engineering, New York University, 1961; Rept. No. AFOSR-553, ASTIA AD No. 257,-019.

Figure 3.—Suggested chair structure for the tetramer of diethyl-fluoroalane tetramer.

atoms have been found. It becomes intuitively obvious that the above chain structures are improbable. Both depict one tricoordinated aluminum atom with an empty 3p orbital at one end of the chain, while the other end aluminum atom is tetracoordinated and has three terminal ligands, at least one of which has the potential for bridging. Such puckered chains should have a strong tendency for ring closure.

We therefore propose that a cyclic eight-membered puckered ring structure best fits the data we have found for the tetramer. Its infrared spectrum shows no ethyl-bridge frequencies. Therefore all the ethyl groups must be terminal on the aluminum atoms, thus accounting for the fact that the pmr spectrum at −60° indicates that all of the ethyl groups are equivalent. Fluorine bridging between the aluminum atoms to give an eight-membered Al–F framework is consistent with the observation that the F^{19} nmr spectrum shows all the fluorine atoms to be equivalent. Such fluorine bridges also are reasonable by analogy to other dialkylhaloalanes, where the halogen, without exception, forms the bridging link.

An interesting analogy can be drawn between diethylfluoroalane and the silicones and dialkylphosphonitriles, all of which are isoelectronic.
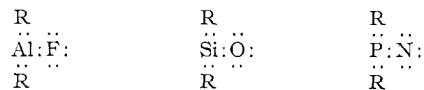
Structural similarities are therefore likely, such as quite stable puckered rings for the tetramers.

Attempts to build scale models for various conformations for eight-membered puckered rings, using tetrahedral bond angles for the alternating aluminum and fluorine atoms, indicate that both crown and tub forms are unfavorable because of great hindrance between the ethyl groups. Chair forms are more favorable, especially if twisted. A still better conformation seems to be the boat form shown in Figure 3, with the four aluminum atoms at the corners of a square and the four fluorine atoms at the corners of a tetrahedron. This affords plenty of room for eight equivalent ethyl groups. This conformation is further improved by

twisting the aluminum atoms out of the square toward the corners of a tetrahedron.

However, extended speculation about the conformation of such puckered rings seems unwise because the assumption of tetrahedral bond angles must be a poor approximation. The very considerable polar character of Al–F bonds must tend to give larger angles for the ring. The H–F–H angle for $(HF)_n$ chain polymers in the gas phase has been reported[14] to be $140 \pm 5°$, and the Si–O–Si bond angle in $[(CH_3)_2SiO]_4$ puckered rings has been found[15] to be $142.5°$ for one crystalline form. It is likely, therefore, that the Al–F–Al bond angles on $[(C_2H_5)_2AlF]_4$ rings are $140°$ or larger.

We have also considered a cubic Al–F framework, analogous to the cubanes, with aluminum pentacoordinated and fluorine tricoordinated. Such unusual coordinations, as well as the highly strained $90°$ bond angles, make this conformation improbable.

It is indeed unfortunate that all efforts to produce crystals of $(C_2H_5)_2AlF$ so far have failed and that low volatility and pyrolysis of this compound when heated have made it impossible to obtain structural information about its vapor phase.

The molecular structure of liquid diethylfluoroalane undoubtedly differs markedly from its structure in solution. Interactions beyond association to a tetramer must be responsible for the extremely high viscosity of the liquid compound at room temperature. The rapid decrease of viscosity upon heating and the high solubility in nonpolar solvents show that such interactions are reversible and rather weak. Two explanations for this may be offered. The polar Al–F units on tetrameric rings may interact with those of neighboring rings to cause a certain random association. Or, on forming the condensed phase, the rings may open to form chains which associate to longer chains, between which considerable random polar interaction may exist. Until more complete data relating the properties of diethylfluoroalane with its structure are available the answer to the question of structure and bonding of this liquid and the extent to which Al–F bridging may occur must remain speculative.

(14) S. H. Bauer, J. Y. Beach, and J. H. Simons, *J. Am. Chem. Soc.*, **61**, 19 (1939).

(15) H. Steinfink, B. Post, and I. Fankuchen, *Acta Cryst.*, **8**, 420 (1955).

The Crystal Structure of Trimethyltin Cyanide

BY E. O. SCHLEMPER AND DOYLE BRITTON

Trimethyltin cyanide forms orthorhombic crystals in space group Cmcm with $a = 9.96$, $b = 11.96$, $c = 6.06$ A, with four molecules per unit cell. The structure consists of planar $(CH_3)_3Sn$ groups with approximately D_{3h} symmetry and disordered cyanide groups symmetrically disposed on either side of the $(CH_3)_3Sn$ groups. The interatomic distances are Sn–C (methyl) $= 2.16 \pm 0.03$, Sn–C (or N) $= 2.49 \pm 0.02$, and C–N $= 1.09 \pm 0.03$. The structure is similar to that of AgCN with infinite chains $(CH_3)_3Sn \cdots CN \cdots (CH_3)_3Sn \cdots CN$, but there appears to be considerable ionic character in the $Sn \cdots CN$ bonds.

As a first step in extending a study of the intermolecular interactions between cyanide nitrogen atoms and potential Lewis acids to compounds of group IV elements, we have determined the structure of $(CH_3)_3$-SnCN. A comparison of the melting points—$(CH_3)_3$-SnCN, $189°$; $(CH_3)_3SnCl$, $38°$; $(CH_3)_3SnBr$, $27°$—suggests some special sort of interaction in the cyanide.

Experimental Section

Preparation and Properties.—Trimethyltin cyanide was prepared in three steps from tin tetrachloride. Tetramethyltin was prepared from $SnCl_4$ and CH_3MgI in *n*-butyl ether by the method of Edgell and Ward.[1] Trimethyltin iodide was prepared from $(CH_3)_4Sn$ and I_2 in benzene by the method of Seyferth.[2] Trimethyltin cyanide was prepared from $(CH_3)_3SnI$ and AgCN in benzene by the method of Seyferth and Kahlen.[3]

The observed melting point, $188.5–188.9°$, and cyanide stretching frequency in $CHCl_3$, 2175 cm^{-1}, agree reasonably well with the reported values[3], $184.5–184.6°$ and 2160 cm^{-1}. The density, measured by flotation in a CCl_4–CBr_4 mixture, was 1.754 ± 0.005 g/cc.

Although $(CH_3)_3SnCN$ is fairly insoluble in benzene and carbon tetrachloride, it is quite soluble in $CHCl_3$. Well-formed, needle-like crystals were obtained by crystallization from $CHCl_3$. By vacuum sublimation very long, thin, flexible needles were obtained. Although $(CH_3)_3SnCN$ is hydrolyzed by water, it was only slowly hydrolyzed by atmospheric moisture (in a Minnesota winter), so that crystals could be handled in air.

Unit Cell and Space Group.—Oscillation, Weissenberg, and precession photographs were taken with Cu Kα (λ 1.5418 A) and Mo Kα (λ 0.7107 A) radiation for rotation about the needle axis (*c* axis). The crystals were orthorhombic with $a = 9.96 \pm 0.02$, $b = 11.96 \pm 0.02$, and $c = 6.06 \pm 0.01$ A. Four molecules per unit cell give a calculated density of 1.746 ± 0.005 g/cc compared to the experimental value of 1.754 ± 0.005 g/cc. Systematic extinctions $h + k$ odd in hkl and l odd in $h0l$ indicated the space group to be Cmc2$_1$, C2cm, or Cmcm. No apparatus was available to test for piezoelectricity. The spoon test described

(1) W. F. Edgell and C. H. Ward, *J. Am. Chem. Soc.*, **76**, 1169 (1954).

(2) D. Seyferth, *J. Org. Chem.*, **22**, 1599 (1957).

(3) D. Seyferth and N. Kahlen, *ibid.*, **25**, 809 (1960).