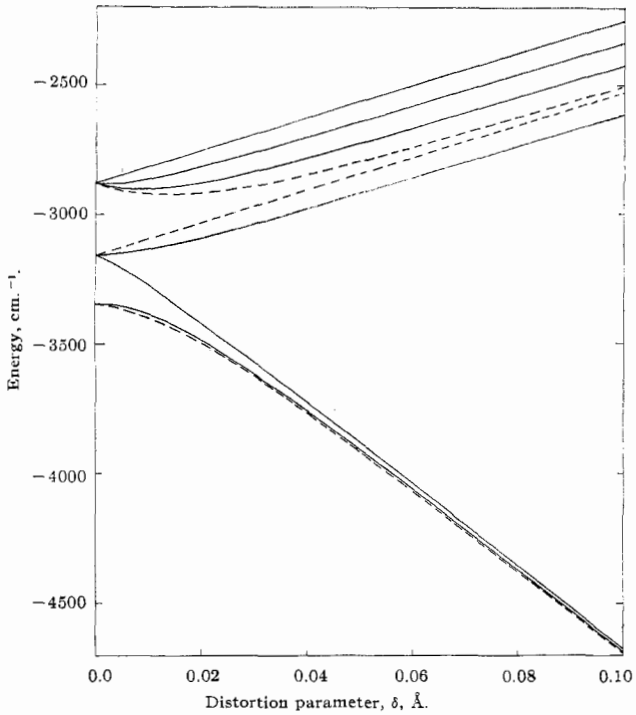

Fig. 4.—The effect of spin–orbit splitting of the $^5T_2$ ground state as a function of the tetragonal distortion. The dashed lines represent nondegenerate states, the solid, doubly degenerate states.

stants greater than about 10 mdynes/Å. the minimum in the potential energy is less than kT at room temperature, about 200 cm.$^{-1}$. Thus thermal averaging of the structure to octahedral symmetry will occur. At lower temperatures the situation is complicated by "antiferromagnetic" distortions. In $KFeF_3$ the resistance to distortion is increased by the lattice energy of the added potassium and fluoride ions.

The absence of distortions about the ferrous ions substituted in cubic MgO[3,5,6] is also explicable in terms of this model. For distortions to occur the ferrous ions would have to do work against the full lattice potential of the crystal since the cations do not cooperate in the distortion.

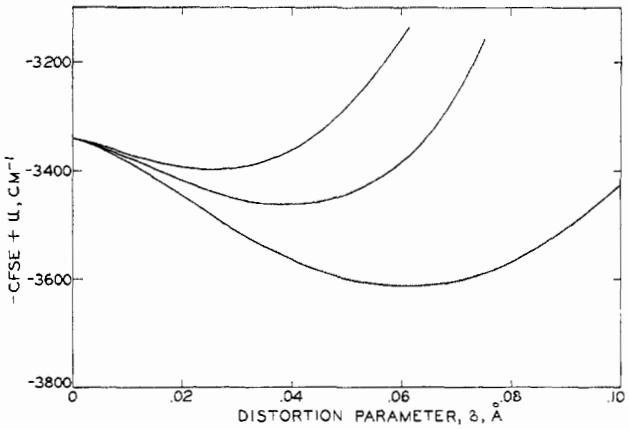

Fig. 5.—Net potential energy (−CFSE + U) as a function of the tetragonal distortion for a variety of force constants. The lower curve is for k = 5 mdynes/Å., the middle curve for 7.5 mdynes/Å., and the top curve for 10 mdynes/Å.

Finally, let us consider the hexaaquoferrous ion. Hush and Pryce[11] have estimated the force constant for the totally symmetric mode to be about 1.12 mdynes/Å. This seems a bit low to us. The force constant for the tetragonal mode is typically about 20% smaller than that of the A_{1g} mode. From a curve such as those shown in Fig. 5 we find that the equilibrium value of δ lies between 0.3 and 0.15 Å. for a force constant between 1 and 2 mdynes/Å. Furthermore, the potential minimum lies well below kT. We conclude that the ferrous ion in aqueous solution should exhibit significant distortion. Crystal structure evidence on this score is meager; it is difficult to sort out distortions due to electronic effects from those of the lattice anions such as SO_4^{2-}. The spectrum of aqueous ferrous ion shows some splitting of the band in the near-infrared,[15] although not as much as the solid fluoride. We believe that a static distortion may account for much if not all of this observed spectral splitting.

(15) F. A. Cotton and M. D. Meyers, *J. Am. Chem. Soc.*, **82**, 5023 (1960).

CONTRIBUTION NO. 970 FROM THE CENTRAL RESEARCH DEPARTMENT AND EXPLOSIVES DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE

Five-Coordinate Stereochemistry

BY E. L. MUETTERTIES, W. MAHLER, K. J. PACKER, AND R. SCHMUTZLER

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N.m.r. data for a series of five-coordinate species are presented and discussed in terms of structure and exchange processes. Trigonal bipyramidal geometry prevails in these compounds, at least for the liquid or solution state, and the more electronegative ligands prefer the axial positions. Intramolecular ligand exchange is a common phenomenon in these structures.

In an earlier article,[1] we presented n.m.r. data for a group of substituted phosphorus(V) fluorides. These data were interpreted in terms of trigonal bipyramidal geometry with occupancy of axial sites by the most electronegative ligands. A case was also made for the susceptibility of five-coordinate structures to fast *intramolecular* positional exchange of ligands. We have now completed a further study of five-coordinate

(1) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

TABLE I

F^{19} N.M.R. DATA FOR 5-COORDINATE P, As, Sb, AND Bi FLUORIDES[a]

Compound	A_{P-F_a}, c.p.s.	A_{P-F_e}, c.p.s.	$A_{F_a-F_e}$, c.p.s.	δ_{F_a}, p.p.m.	δ_{F_e}, p.p.m.	A_{HF_a}, c.p.s.	A_{HF_e}, c.p.s.
$(C_2H_5)_2NPF_4$ (25°)	851		...	−10		...	...
$(C_2H_5)_2NPF_4$ (−85°)	793	916	70	−17.3	−5.2	...	...
$C_2F_5PF_4$	1175		...	−15.8		...	...
$[(C_2H_5)_2N]_2PF_3$	751	875	46	−17	−9	...	...
Cl_2PF_3 (25°)	1050		...	−112		...	...
Cl_2PF_3 (−130°)	1023	1085	142	−144	−36	...	...
Br_2PF_3	1040		...			...	...
$(C_2F_5)_2PF_3$	1245		...	−21		...	...
$C_6H_5PF_3H$	831	969	31.5	−46	9.7	124	31.5
$C_6H_5PF_3Cl$	956	1035	80	−89	−23	...	...
$C_6H_5PF_3N(CH_3)_2$	820	955	55	−36	−9	...	...
$C_6H_5PF_3N(C_2H_5)_2$	815	955	56	−35	−11	...	...
$C_2H_5PF_3N(C_2H_5)_2$	825	985	51	−37	−8	11	...
CF_3SF_3			68	−127	27		
$C_6H_5AsF_4$	...	...	...	−14	(30)	...	...
$(C_6H_5)_2AsF_3$	...	...	67	−8.4 (90)	13.9 (90)	...	...
$(C_6H_5)_3AsF_2$	...	...	...	8 (1)	...	...	...
$(C_6H_5)_3SbF_2$	...	...	...	58 (12)	...	...	...
$(C_6H_5)_3SbFCl$	...	...	...	73 (13)	...	...	...
$(C_6H_5)_3BiF_2$	...	...	...	81 (20)	...	...	...

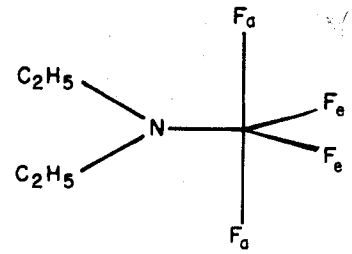
[a] The number in parentheses after δ values for compounds containing quadrupolar nuclei (As, Sb, and Bi) are the line widths at half-height.

compounds, the results of which are discussed below.

(A) $(C_2H_5)_2NPF_4$.—At 25°, the F^{19} n.m.r. spectrum of $(C_2H_5)_2NPF_4$ comprises two peaks of equal intensity. The doublet arises from PF spin–spin coupling as shown by the insensitivity of the doublet separation to frequency (40 and 56.4 Mc.) of the n.m.r. measurement. On cooling of the sample, the doublet gradually broadens and eventually breaks into two doublets, each line of which gains triplet fine structure. These data establish a structure in which there are two fluorine atom environments each of which contains two fluorine atoms.

The bulk properties of $(C_2H_5)_2NPF_4$ are consistent with a simple monomer; however, it might be argued that the low-temperature spectrum arises from a dimeric or polymeric species and that the temperature dependence of the F^{19} spectrum reflects the varying rate of polymer dissociation. We find, however, the coalescence temperatures of the F^{19} spectrum to be identical for pure $(C_2H_5)_2NPF_4$ and for its solution in various hydrocarbons. Thus, the dynamic process that leads to spectroscopic equivalence at 25° is an intramolecular one. Moreover, the sets of PF coupling constants (Table I) derived from the low-temperature spectrum fall into an acceptable range for typical five-coordinate PF compounds[1] and well outside the range found for octahedral PF structures.[2] The PF coupling constant calculated by averaging the two low-temperature (−85°) values is 855 c.p.s. as compared with the observed value at 25° of 851 c.p.s.; thus, no gross structural changes can have occurred across this temperature span.

If a geometry closely approximating a trigonal bipyramid prevails in $(C_2H_5)_2NPF_4$, then there are only two possible geometrical isomers. Apical substitution may be ruled out since in no way could a 2:2 fluorine atom environment be generated. The equatorial isomer **1** fits very nicely for a static situation.



1

Earlier it was established that the n.m.r. resonance for axial fluorine atoms occurs at significantly lower fields than that for the equatorial fluorines and that the axial fluorine atoms exhibit a much lower PF coupling constant than the equatorial fluorine atoms.[1] The n.m.r. parameters for an equatorial $(C_2H_5)_2NPF_4$ conform to these observations and, moreover, the values of A_{PF_e} and A_{PF_a} are within the range established in our earlier studies.[1] Alternatively, tetragonal pyramidal geometry may prevail. However, the observed differences in the directly bonded PF coupling constants seem too large for any spatial effect due to a far removed ethyl group. Therefore, we favor the equatorially-substituted trigonal bipyramidal model.

Analysis of the n.m.r. transition region sets a value of 6–12 kcal./mole to the activation energy for fluorine exchange in $(C_2H_5)_2NPF_4$. Our spectroscopic data provide no information about the exchange other than the fact that the process is intramolecular. Intramolecular fluorine exchange in $(C_2H_5)_2NPF_4$ does require both rotation about the P–N bond and PF_4 bending (*cf.* argument for PF_5[3] and XPF_4.[1] There is the possibility that the observed barrier largely

(2) E. L. Muetterties, T. A. Bither, M. Farlow, and D. D. Coffman, *J. Inorg. Nucl. Chem.*, **16**, 52 (1960).

(3) S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

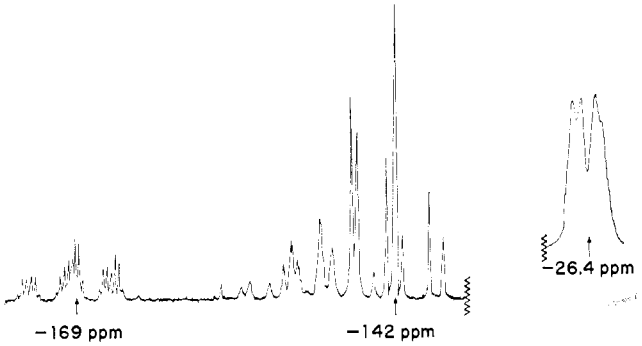
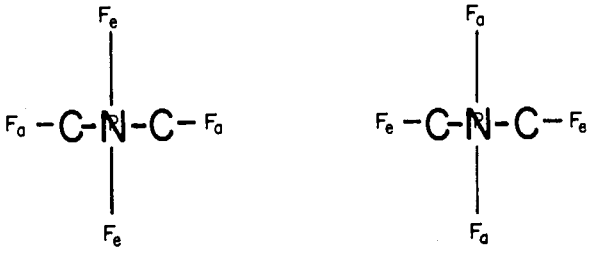


Fig. 1.—The F^{19} spectrum of F_4SNCF_3 at −104° obtained at 56.4 Mc. The multiplet to the right represents the CF resonance, and the multiplets to the left represent the SF resonances.

reflects that of interconversion of such rotational isomers as **2** and **3**.[4] Since rotation alone cannot de-

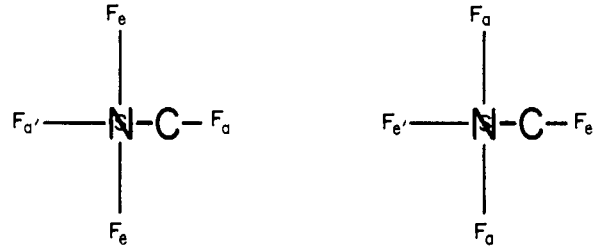


2 **3**

label the PF fluorine atoms, there must be a lower barrier to the PF_4 bending mode. Conversely, the observed barrier may largely relate to the PF_4 bending mode. Actually it is probably unrealistic to dissociate these two modes from each other in any description of the traversing of the potential energy surface in $(C_2H_5)_2NPF_4$.

(B) **$CF_3N{=}SF_4$.**—The F^{19} spectrum of $CF_3N{=}SF_4$[5] at 25° consists of a CF_3 quintet and an SF_4 multiplet. Spectroscopic equivalence of SF fluorine atoms is removed at temperatures below −80° where a complex pattern arises (Fig. 1) that has the general appearance of an AB_2X, or more properly AB_2XR_3, spectrum. Thus there are three different fluorine atom environments in $CF_3N{=}SF_4$. The exchange process apparent from the temperature dependence of the n.m.r. spectrum must be intramolecular because F_C–F_S coupling is preserved at elevated temperatures and the n.m.r. coalescence temperatures are the same for pure $CF_3N{=}SF_4$ and its solutions in organic solvents. Approximate analysis of the n.m.r. exchange region sets an order of magnitude of 6 kcal./mole to the activation energy.

To gain such low symmetry at low temperatures in the n.m.r. experiment, as to have three different fluorine atoms, necessitates restricted rotation about the S–N bond. For reasons identical with those advanced for $(C_2H_5)_2NPF_4$ above, we suggest that these n.m.r. data are best rationalized in terms of trigonal bipyramidal geometry with the CF_3N group at an equatorial position. Possible rotation isomers are **4** and **5**. Very fast equilibration of the ground state

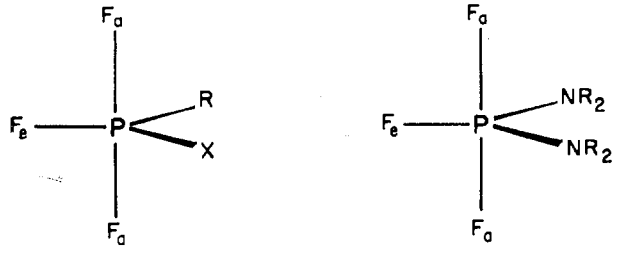


4 **5**

with an excited state of essentially tetragonal pyramidal geometry is again a necessary postulate to account for the n.m.r. equivalence of SF fluorine atoms at 25°, and the mechanism probably consists of some combination of a vibrational and a rotational mode as proposed for $(C_2H_5)_2NPF_4$.

(C) **$C_2F_5PF_4$.**—Like CF_3PF_4,[1] the ethyl derivative shows only one chemically-shifted PF resonance with PF and F_CF_P spin coupling invariant over a wide temperature range. These data are consistent with an apically-substituted tetragonal pyramid or with trigonal bipyramidal geometry in which there is fast intramolecular[1] fluorine exchange.

(D) **RPF_3X and X_2PF_3.**—The F^{19} n.m.r. spectra (Table I) of a series of compounds of the type RPF_3X, where R is C_6H_5 or C_2H_5 and X is H, Cl, or NR_2, and of $(R_2N)_2PF_3$ all show nonequivalence of fluorine atoms. For example, the F^{19} n.m.r. spectrum of $C_6H_5PF_3$-$N(C_2H_5)_2$ consists of pairs (PF splitting) of doublets and triplets of relative intensities 2 and 1, respectively. These data alone do not permit an unequivocal selection of a stereoisomer. However, it was earlier established for a number of aryl and alkyl derivatives of PF_5 that A_{PF} and δ_F are consistently larger for equatorial PF than for apical PF. Therefore, based on the data in Table I, we assign equatorial substitution, **6** and **7**, to these derivatives.[6]



6 **7**

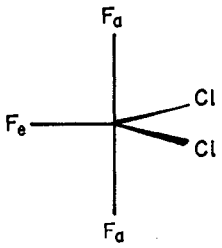
$(C_2F_5)_2PF_3$, like $(CF_3)_2PF_3$[1], showed only one type of P–F fluorine environment down to −120°. The PF and F_PF_C spin-coupling constants were invariant over the temperature range −120 to 50°.

(4) Lack of dimerization or polymerization in $(C_2H_5)_2NPF_4$ suggests the existence of $p\pi$–$d\pi$ overlap in the PN bond. A formally analogous class of compounds, the aminoboranes R_2NBR_2, have this potential for π-bonding and certain members of this class do show evidence in the n.m.r. experiment of restricted BN rotation with barriers in the range of 15–20 kcal./mole: G. E. Ryschkewitsch, W. S. Brey, Jr., and A. Saji, *J. Am. Chem. Soc.*, **83**, 1010 (1961); P. A. Barfield, M. F. Lappert, and J. Lee, *Proc. Chem. Soc.*, 421 (1961).

(5) This compound boils at +1° and displays no bulk properties suggestive of association: C. W. Tullock, D. D. Coffman, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 357 (1964).

(6) Distinction between trigonal bipyramid and tetragonal pyramid for the C_{2v} model is not meaningful. Nevertheless, we prefer to consider these in the context of trigonal bipyramidal geometry with the presumption that the F_aPF_a angle will not be grossly smaller than 180°.

As reported earlier,[1] there is spectroscopic nonequivalence of fluorine atoms in Cl_2PF_3 at temperatures below $-115°$ (petroleum ether solution). We now have a rough estimate of the activation energy for this intramolecular[7] exchange process by analysis of the exchange broadening of the n.m.r. lines over the temperature range -100 to $-150°$; the value is 6.5 ± 2 kcal./mole. The F^{19} spectrum of Br_2PF_3 is similar to that of Cl_2PF_3. At 25°, there is spectroscopic equivalence; the spectrum consists of a simple doublet. On cooling below $-100°$, the doublet broadens and begins to merge but crystallization of solvent (CCl_2F_2) precluded lower temperature studies. We conclude that Br_2PF_3 is isostructural (**8**) with Cl_2PF_3[1] and that the barrier to intramolecular fluorine exchange is lower in Br_2PF_3.



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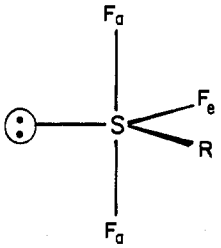
(E) **SF_4 Derivatives.**—Rosenberg and Muetterties[8] and Sheppard[9] have presented n.m.r. data for a number of perfluoroalkyl derivatives of sulfur tetrafluoride, and more recently we have examined the F^{19} n.m.r. spectrum of CF_3SF_3. In the case of the monoderivatives, i-$C_3F_7SF_3$,[8] $C_6H_5SF_3$,[9] and CF_3SF_3, there are two fluorine atom environments, which is consistent with either structure **9** or **10**. As we had noted earlier in the alkyl and aryl fluorophosphoranes, the F^{19} reso-



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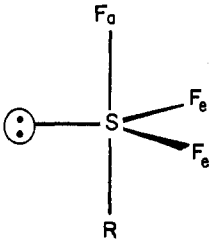


10

nances of apical fluorine atoms always lie at much lower fields than do those of equatorial fluorine atoms. Significantly, the doublet resonance of $C_6H_5SF_3$ is 98 p.p.m. to the low-field side of the triplet; in i-$C_3F_7SF_3$ the SF_2 multiplet is 115 p.p.m. to low field of the SF multiplet, and in CF_3SF_3 the SF_2 multiplet is 100 p.p.m. to low field of the SF triplet. These chemical shift data would tend to favor structure **9** over **10**.

In $(i\text{-}C_3F_7)_2SF_2$ and $(i\text{-}C_3F_7)(CF_3)SF_2$, the fluorine atoms are spectroscopically equivalent and the F^{19} spectra are temperature independent. For these two compounds, the position of the SF_2 resonance is intermediate between the positions of the SF_2 and SF resonances of i-$C_3F_7SF_3$, providing no selection between fluorine atoms at apical or equatorial positions. We suggest that since R_f–R_f repulsions should be very large, fast positional exchange analogous to that found for Cl_2PF_3 may well be occurring in these two molecules and the reported n.m.r. parameters may be averaged values for the two extreme models. If this dynamic picture is assumed and the δ_{F_a} and δ_{F_e} values of i-$C_3F_7SF_3$ are employed, the calculated average for δ_F is -58 p.p.m. as compared to the observed values of -57 and -54 p.p.m. for $(i\text{-}C_3F_7)_2SF_2$ and $(i\text{-}C_3F_7)$-CF_3SF_2, respectively. This close agreement may be fortuitous, but we favor the dynamic positional exchange picture for these two derivatives.

(F) **Arsenic, Antimony, and Bismuth Derivatives.**—We have confirmed our earlier report[10] that the F^{19} n.m.r. spectrum of AsF_5 consists of a single broad peak; line shape is not grossly altered in going from neat AsF_5 samples to solutions in aromatic hydrocarbons and chlorofluorocarbons, nor is line shape significantly temperature dependent. Line breadth is ascribed to quadrupole relaxation effects and the spectroscopic equivalence of fluorine atoms to intramolecular ligand exchange analogous to that in PF_5.[3]

Like the R_3PF_2 compounds, the R_3MF_2 class wherein M is arsenic, antimony, or bismuth shows n.m.r. spectroscopic equivalence of fluorine atoms. The spectra are essentially temperature independent. Line widths are surprisingly sharp (all the central nuclei here have large quadrupole moments) and the resonances are shifted to rather high fields (Table I). Chemical shift is relatively insensitive to solvent and concentration. For example, the F^{19} chemical shift for $(C_6H_5)_3BiF_2$ changed by 2 p.p.m. increments in going from a 9:1 CH_3OH:$CHCl_3$ medium to chloroform to toluene. Cryoscopic studies showed that these difluorides are all monomers in benzene solution. These data are consistent with but do not establish a trigonal bipyramid structure with axial fluorine atoms. Such geometry has been established for $(CH_3)_3SbX_2$ where X is Cl, Br, and I.[11]

The F^{19} spectrum of $C_6H_5AsF_4$ consists of a single relatively sharp (30 c.p.s. half-width) peak at $+14$ p.p.m. Toluene dilution of the neat sample did not significantly shift the resonance position. This is thus analogous to the general results for XPF_4 derivatives[1] in that there is spectroscopic equivalence of fluorine atoms. Absence of AsF hyperfine structure is attributed to relatively fast quadrupole relaxation. Fast intermolecular fluorine exchange due to hydrogen fluoride impurity is ruled out by the experimental finding that line shape was not affected by addition of sodium fluoride to the sample, but fast intramolecular fluorine exchange may be occurring through an associative mechanism.

(7) The n.m.r. temperature dependence cannot be due to association to dimer or polymer. The bulk properties of Cl_2PF_3 give no suggestion of association at 10°. Since the PF coupling constant of 1050 c.p.s. at 25° is so similar to the average of 1044 c.p.s. for the observed low temperature PF constants, there can be no significant structural changes within this temperature range.

(8) R. M. Rosenberg and E. L. Muetterties, *Inorg. Chem.*, **1**, 756 (1962).

(9) W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3058 (1962).

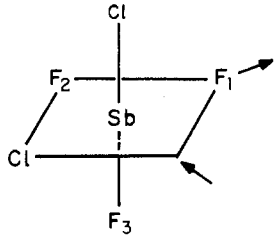
(10) E. L. Muetterties and W. D. Phillips, *ibid.*, **81**, 1084 (1959).

(11) A. F. Wells, *Z. Krist.*, **99**, 367 (1938).

The F^{19} spectrum of $(C_6H_5)_2AsF_3$ in toluene solution consists of a doublet and triplet of relative intensity 2 and 1. The spectrum is invariant over large changes in temperature and in concentration. These n.m.r. data are identical with those described for dialkyl- and diarylphosphorus trifluorides, and accordingly we assign a slightly distorted trigonal bipyramidal structure with equatorial aryl groups to this arsenic compound.

Surprisingly, $(CH_3)_2AsF_3$ unlike $(C_6H_5)_2AsF_3$ or $(CH_3)_2PF_3$ shows evidence of association. It is a colorless crystalline compound that melts at 85° and in contrast to all the other alkyl and aryl derivatives of P, As, Sb, and Bi, it is not very soluble in aromatic hydrocarbons. Solutions sufficiently concentrated for the n.m.r. experiment were obtained only with strong donor solvents such as acetone and acetonitrile. These solutions gave a single F^{19} resonance at 25° and doublet–triplet resonances at low temperatures. The low-temperature spectrum is believed to be representative of an octahedral $(CH_3)_2AsF_3\cdot$ donor species rather than a five-coordinate structure. The anomalous behavior of this methyl derivative is to be explored further.

Kolditz and Lieth[12] have prepared SbF_3Cl_2 by reaction of SbF_3 and Cl_2 and have suggested that this derivative of SbF_5 is structurally $SbCl_4^+SbF_6^-$. More recently, Dehnicke and Weidlein[13] have proposed, on the basis of a Raman and infrared study, that SbF_3Cl_2 is a monomeric trigonal bipyramid of D_{3h} symmetry with chlorine atoms at axial positions. Consideration of SbF_3Cl_2 as a monomeric species is untenable except possibly at very high temperatures in the gas phase because it is a crystalline solid melting at 68° to a very viscous liquid. This behavior is analogous to SbF_5, an associated species in which the antimony atom is hexacoordinated through bridge fluorine atoms. We find that the F^{19} n.m.r. spectrum of a supercooled mixture of SbF_3Cl_2 and chlorine is a single, broad line at 25°. On cooling, three discrete broad peaks of roughly equal intensity became discernible. Again, this behavior parallels that of the parent $(SbF_5)_x$[14] and we suggest that SbF_3Cl_2, at least in the solution and molten states, is present primarily as an associated species with hexacoordinate antimony and bridging chlorine or fluorine atoms. A possible repeating unit is structure **11**.



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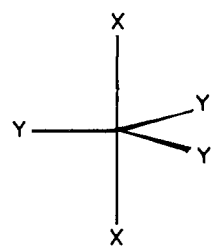
Pentamethylantimony exhibits a single sharp proton resonance at τ 9.3 with a half-height line width of 1.5 c.p.s. Solutions of $Sb(CH_3)_5$ in carbon disulfide display a single proton resonance down to $\sim -100°$. Spectroscopic equivalence of methyl groups might arise here from a fast intermolecular exchange of methyl groups as observed for aluminum trimethyl or by an intramolecular process analogous to that postulated for PF_5.[3] We favor the latter alternative but can back our preference with no convincing arguments. The proton spectrum of the closely related pentaphenylphosphorus is complex; there are no obvious large proton shifts that might suggest nonequivalence of aryl groups.

(G) **Conclusions.**—In the first article,[1] we suggested that in a trigonal bipyramidal stucture the most electronegative ligands would always assume apical positions. The compounds examined in this present study are consistent with this rule. The variation in ligand type examined is large: H, alkyl, aryl, Cl, R_2N, CF_3, and C_2F_5.[15] In all cases of the substituted phosphorus fluorides the more electronegative fluorine atoms appear at apical positions; never do the less electronegative groups assume apical positions. This rule also holds for all trigonal bipyramidal structures that have been investigated and reported in the literature:[16] SF_4[17]; ClF_3[18]; F_4SO[19]; $(CH_3)_2TeCl_2$[20]; $(C_6H_5)_2TeBr_2$[21]; $(CH_3)_3SbX_2$,[11] X = Cl, Br, I; $(CH_3)_3Sn(Cl)NC_5H_5$[22]; $[(CH_3)_3Sn(NH_3)_2]^+$[23]; $(CH_3)_3SnF_2$ [in $(CH_3)_3SnF$, $(CH_3)_3SnSbF_6$, and $(CH_3)_3SnAsF_6$][24,25]; $[(CH_3)_3N]_2AlH_3$[26]; and $[(C_6H_5)_3P]_2Fe(CO)_3$.[27] It is probable that the general rule for trigonal pyramidal stereochemistry will ultimately be met by an exception. Perhaps the most favorable case is X_2MY_3 where Y–Y repulsions are so large that even though Y is more electronegative than X the geometry shown in structure **12** will prevail. This might be the situation in $(CF_3)_2$-



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(15) The CF_3 group in $(CF_3)_3PF_2$ is equatorial; however, the n.m.r. data for CF_3PF_4 and $(CF_3)_2PF_3$ are equivocal with respect to stereochemical conclusions. The same applies to the C_2F_5 derivatives.
(16) We also wish to note that tetragonal pyramidal geometry has never been established for a five-coordinate d^0 or d^{10} species with monodentate ligands in the gaseous, liquid, or solution state.
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PF_3 and $(C_2F_5)_2PF_3$, which do show n.m.r. spectroscopic equivalence of PF fluorine atoms. Recently, it has been shown that the triphenylphosphine groups in $[(C_6H_5)_3P]_3RhHCO$ are at equatorial positions.[28] The seemingly anomalous position of the hydrogen atom at an apical site may, in fact, be a reflection of large repulsions between $(C_6H_5)_3P$ groups.

The low barrier to intramolecular exchange in Cl_2PF_3 makes a stronger case for our earlier contention that positional exchange will be a common, low-energy process in five-coordinate structures. Primarily this is a reflection of the small energy difference between a trigonal bipyramid and a tetragonal pyramid. We feel that, in general, a trigonal bipyramid or a slightly distorted version of it will best describe the ground state for five-coordinate species with monodentate ligands (gaseous, solution, or liquid state)[29] with a close-lying vibronically-excited state of tetragonal pyramid geometry. The potentially facile process for intramolecular ligand exchange in five-coordinate structures makes it unlikely that geometrical isomers in a substituted MX_5 species could be isolated by conventional techniques. It is notable that the very sensitive n.m.r. technique has given no evidence of isomers in our present and earlier work.[1] Moreover, gas chromatographic analysis of the various alkyl- and arylphosphorus(V) fluorides has failed to give evidence of geometrical isomers.

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(29) Packing forces in the solid state may be large with respect to the energy difference between a trigonal bipyramid and a tetragonal pyramid. Therefore, there is the possibility that the geometry in the solid state may differ from that in the liquid or gasous state.

Experimental

All F^{19} spectra were recorded at 56.4 Mc. on a Varian Model V4300 high resolution spectrometer and associated magnet, and the H^1 spectra on a Varian A-60 spectrometer. Calibration of spectra was effected by superposition of an audiofrequency on the sweep field to produce side-band peaks. The external reference, for the F^{19} spectra, was trifluoroacetic acid.

All of the compounds described in this report were prepared by literature procedures and purified by distillation or recrystallization. Transfer of all volatile reagents was effected in a vacuum system. The synthesis of the compounds $(C_2H_5)_2NPF_4$ and $[(C_2H_5)_2N]_2PF_3$ will be reported separately.[30]

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(30) R. Schmutzler, to be published.

CONTRIBUTION FROM THE WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON, W.C.1., ENGLAND

The Crystal Structure of Dibromo-2,5-dimethylpyrazinenickel(II) ($NiBr_2(CH_3)_2N_2C_4H_2$)

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The crystal structure of the bright purple diamagnetic compound dibromo-2,5-dimethylpyrazinenickel(II) has been analyzed from two-dimensional X-ray diffraction data. Crystals are monoclinic, space group C2/m, a = 9.09, b = 8.20, c = 6.52 Å., β = 108° 36′, two formula units per unit cell. The structure consists of infinite chains of (2,5-dmp)$NiBr_2$ along the c-axis, the nickel atoms being linked to each other *via* the nitrogen atoms of the pyrazine ring. The coordination of the nickel atom is square-planar with nickel site symmetry 2/m. The bromine atoms are 2.31 Å. from the nickel atom along the twofold axis (b) perpendicular to the plane of the pyrazine groups.

Introduction

As part of a general study of pyrazine metal compounds, Lever, Lewis, and Nyholm[1] have recently prepared three intensely colored diamagnetic nickel(II) compounds. These are the compounds dibromo-2,5-dimethylpyrazinenickel(II) ((2,5-dmp)$NiBr_2$) and diiodo-2,5-dimethylpyrazinenickel(II), which are an intense purple color, and the analogous compound diiodo-2,6-dimethylpyrazinenickel(II), which is black. The compounds are diamagnetic, which would indicate that the coordination of the nickel atom is square-planar.[2]

Because most square-planar compounds of nickel(II) are yellow or red, it had been suggested that the intense color might result from a tetrahedral configuration, and, as pointed out by Lever, Lewis, and Nyholm,[1] the two configurations cannot be distinguished by means of the diffuse reflectance spectra. An X-ray diffraction analysis of (2,5-dmp)$NiBr_2$ was initiated in order to establish the molecular stereochemistry.

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(2) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960.

Experimental

The crystals decompose very rapidly in the presence of water vapor, and it was necessary to seal each crystal in a Lindemann glass capillary in a P_2O_5 drybox. This did not completely eliminate crystal degradation, but the rate was much reduced and changes as reflected in the apparent thermal parameters occurred only over periods of some weeks. Crystals of the compound show striking dichroism from purple to wine-red in, respectively, reflected and transmitted light.

Crystals are monoclinic, space group C2/m, a = 9.09 ± 0.01, b = 8.20 ± 0.01, c = 6.52 ± 0.01 Å., β = 108° 36′, Z = 2 mole-