

## Vibrational Spectra and Structure of Tetrakis(trifluoromethyl)hydrazine in the Crystalline and Fluid States

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Received March 2, 1972

The infrared spectra of solid and gaseous tetrakis(trifluoromethyl)hydrazine have been recorded from 1600 to 33  $\text{cm}^{-1}$ . The Raman spectra of the gas, liquid, and solid have also been recorded and depolarization values have been measured. A comparison of the vibrational spectra in the solid and fluid states indicates that the molecule exists in only one conformer in all three physical states. A similar comparison of the frequencies for the infrared and Raman bands shows the mutual exclusion principle is not operative, and it is concluded that the  $\text{N}_2(\text{CF}_3)_4$  molecule exists in only the gauche,  $C_2$ , structure. Assignments of the observed frequencies to the normal vibrations based on the depolarization values, band positions, and relative intensities are presented for the molecule in the  $C_2$  configuration. The results are compared to those obtained for other  $\text{X}_2\text{Y}_4$  molecules of the group Va elements.

### Introduction

The symmetry of molecules which have the general formula  $\text{X}_2\text{Y}_4$  has been the subject of several recent vibrational studies from this laboratory.<sup>1-7</sup> It has been found that of the several possible structures only the trans ( $C_{2h}$  symmetry) and gauche ( $C_2$ ) structures are present when the central pair of atoms is a group Va element. These structures correspond to a pyramidal arrangement of neighboring atoms and nonbonded electron pairs about the central group V atoms. The relative amounts of the trans or gauche isomers will depend upon the interactions of the two nonbonded electron clouds and the steric repulsions of the substituent atoms, as well as other less important forces.<sup>8</sup>

Although the N-N bond is the shortest of the X-X bonds of the group Va elements, the substituted hydrazines have been shown to have a much greater predominance of the gauche isomer compared to the trans form in relation to the corresponding phosphorus compounds. For example, we have recently shown<sup>9</sup> that tetramethylbiphosphine in the fluid states is approximately 40% trans whereas the corresponding substituted hydrazine has been reported<sup>9</sup> to be all in the gauche form. Similarly, tetrafluorohydrazine has been shown<sup>2,10,11</sup> to be composed of a 53-47% mixture of the trans and gauche isomers, respectively, at ambient temperature, although in the initial electron diffraction study<sup>12</sup> the trans isomer was missed. The corresponding phosphorus compound has been reported<sup>13</sup> to be all in the trans form. Thus, even though the steric factors should be the more pronounced for the substituted hydrazines, the gauche isomer appears to be

the most stable for the nitrogen-containing compounds. Therefore, we have investigated the vibrational spectrum of  $\text{N}_2(\text{CF}_3)_4$  in both the fluid and solid states in order to determine the symmetry and normal vibrations of this molecule.

An electron diffraction study of  $\text{N}_2(\text{CF}_3)_4$  has been reported,<sup>14</sup> but this work was done prior to any structural work which indicated the substituted hydrazines might have  $C_{2h}$  symmetry. Therefore, Bartell and Higgenbotham<sup>14</sup> assumed the molecule had  $C_2$  symmetry for the structural refinements. In fact, these authors concluded that configuration around the nitrogen was approximately planar and that the dihedral angle approached  $90^\circ$  so the molecule has nearly  $D_{2d}$  symmetry. Since we have shown that the presence of two X-X stretching modes is a convenient method for the detection of two isomers and the rule of mutual exclusion between the infrared and Raman frequencies is rather conclusive for the determination of the  $C_{2h}$  or  $D_{2h}$  symmetry, we felt that the verification of the symmetry for the  $\text{N}_2(\text{CF}_3)_4$  by another technique was quite desirable. Also, the question of the symmetry of this molecule in the crystalline state was still unanswered. Thus, we are reporting the results of our infrared and Raman spectral studies of this molecule.

### Experimental Section

The sample of  $\text{N}_2(\text{CF}_3)_4$  was donated by Professor John A. Young, and was used without further purification.

The infrared spectra were recorded from 1600 to 250  $\text{cm}^{-1}$  with a Perkin-Elmer Model 621 spectrophotometer. The atmospheric water vapor was removed from the spectrophotometer housing by flushing with dry air. In the higher frequency region, the instrument was calibrated with standard gases.<sup>15</sup> The lower wave number region was calibrated by using atmospheric water vapor and the frequencies reported by Hall and Dowling.<sup>16</sup> The spectrum was recorded with the gaseous sample contained in a 20-cm cell equipped with CsI windows. The spectrum of the solid was obtained by condensing the sample on a CsI plate maintained at  $-190^\circ$  with boiling nitrogen. Representative mid-infrared spectra are shown in Figures 1 and 2.

The Raman spectrophotometer used was a Cary Model 82 equipped with both He-Ne and argon ion laser sources. The Raman spectrum of the gas was measured at  $25^\circ$  in a standard Cary multipass gas cell using a CRL Model 53B argon ion laser source. The spectrum of the room temperature liquid was

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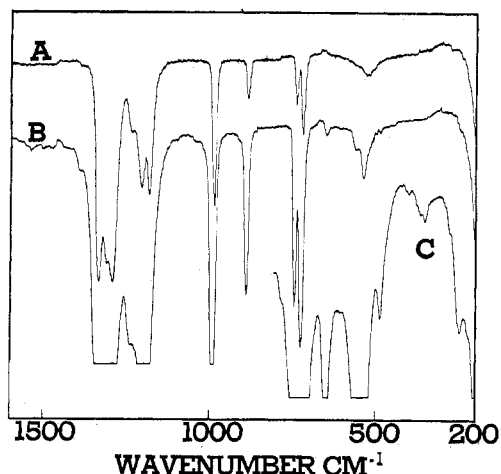


Figure 1.—Mid-infrared spectrum of gaseous  $N_2(CF_3)_4$  at the following pressures and 20-cm path lengths: A, <1 Torr; B, 2 Torr; C, 150 Torr.

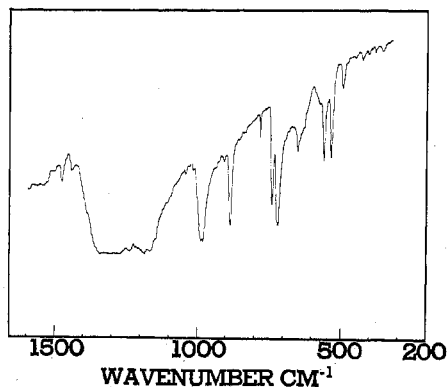


Figure 2.—Mid-infrared spectrum of solid  $N_2(CF_3)_4$ .

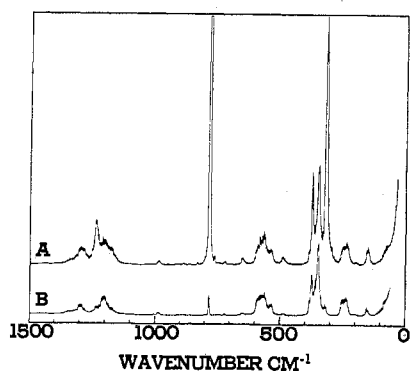


Figure 3.—Raman spectrum of liquid  $N_2(CF_3)_4$  at 25°. A represents parallel polarization. B represents perpendicular polarization.

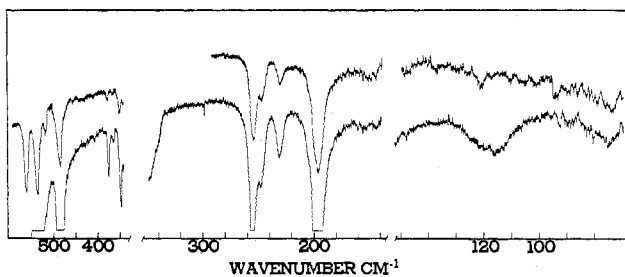


Figure 4.—Far-infrared spectrum of solid  $N_2(CF_3)_4$  of various thicknesses.

taken with the sample sealed in a capillary tube. The spectrum of the sample at temperatures below room temperature and the spectrum of the solid sample ( $-90^\circ$ ) were obtained by using a cell which was identical in design with that reported by Miller and Harney.<sup>17</sup> Depolarization measurements in the liquid phase were made by using the analyzer method. A polarization scrambler was inserted between the analyzer and the monochromator when making depolarization measurements. Representative Raman spectra are illustrated in Figure 3.

The far-infrared spectrum was recorded from 33 to 590  $cm^{-1}$  (see Figure 4) on a Beckman Model IR-11 spectrophotometer. The instrument was purged with dry nitrogen and calibrated with the frequencies reported for water vapor by Hall and Dowling.<sup>16</sup> For the spectrum of the gas phase in this frequency region, a Beckman variable-path-length cell equipped with polyethylene windows was used. The cell used for recording the spectrum of the solid at  $-190^\circ$  has been described earlier.<sup>1</sup> The frequencies for all observed bands are expected to be accurate to  $\pm 2 cm^{-1}$ . These frequencies are listed in Table I with their relative intensities and proposed assignments.

### Results

A comparison of the Raman spectra of  $N_2(CF_3)_4$  in the gas, liquid, and solid phases reveals essentially no change in the number of bands present or their relative intensities. Likewise, the infrared spectra of the gaseous and solid material (see Figures 1 and 2) are essentially identical. Since the frequencies of the skeletal stretching and bending motions are expected to show significant variation with changes in molecular structure, particular attention was paid to these vibrational modes. For example, the  $786-cm^{-1}$  band in the Raman spectrum (later assigned as the N-N skeletal stretching mode) was recorded at a spectral slit width of approximately  $2 cm^{-1}$  over a wide temperature range, from 25 to  $-190^\circ$ . No change in frequency or intensity was observed for this band, nor were any bands observed to appear or disappear as the molecule solidified. Therefore, one must conclude that the molecule exists in only one conformer in all three physical states.

Previous studies have shown that when the central atoms present in an  $X_2Y_4$  molecule are group Va elements, only the trans ( $C_{2h}$  symmetry) and gauche ( $C_2$  symmetry) structures are possible. However, because of the electron diffraction study of  $N_2(CF_3)_4$ , the possibility of  $D_{2d}$  was also considered. For the trans structure the mutual exclusion principle is operative, whereas for the gauche structure all bands are allowed in both the infrared and Raman spectra. For the molecular symmetry  $D_{2d}$ , the vibrations of species  $a_1$  and  $b_1$  are Raman active only whereas those of species  $b_2$  and  $e$  are active in both spectra. Examination of the infrared and Raman spectra reveals a large number of coincidences. To be sure, some of these coincidences are expected (even for the trans structure) because of possible accidental degeneracies of the  $CF_3$  motions. However, in all but a few cases, a band which appears in the infrared also has a Raman counterpart. Two exceptions are perhaps worth noting, since they involve strong Raman bands. The strongest Raman band occurs at  $786 cm^{-1}$  in all three phases. In the infrared spectrum of the gas phase, a weak shoulder on the strong  $741-cm^{-1}$  band is observed at  $785 cm^{-1}$ . In the solid phase a sharp, weak band appears at  $783 cm^{-1}$ . One might suspect that this is an example of mutual exclusion. However, since the band is reasonably assigned as the N-N stretching vibration, it is not surprising that only a small dipole moment change occurs

TABLE I<sup>a</sup>  
 INFRARED AND RAMAN SPECTRA OF TETRAKIS(TRIFLUOROMETHYL)HYDRAZINE

Ir			Raman					Assignment		
Gas Freq, cm <sup>-1</sup>	Solid Freq, cm <sup>-1</sup>	Rel Intens	Gas Freq, cm <sup>-1</sup>	Liquid Freq, cm <sup>-1</sup>	Rel Intens	Polarization	Solid Freq, cm <sup>-1</sup>			
1333	1335	s		1334		4		1326	CF <sub>3</sub> str	
1310	1308	s								
1292			1297	1295		3				
	1270	s		1278		2				
			1246	1239		9	p			1240
1232	1234	s								
			1210	1213		4				
1205	1205	s		1203		4				1205
1180	1181	s		1176		3				1177
	1162	s								
987	987	vs		987		2	dp		NC <sub>2</sub> antisym str	
	979									
	905		vvw							
886	885	s		889		1	dp		NC <sub>2</sub> antisym str	
				864		1	p			
				832		2	p	830	NC <sub>2</sub> sym str	
785 sh	783	w	786	786	100	p	786	N-N str		
				764		2	p			
741	740	s		752		1	p		724	
722	721	s		724		2	p			
650	652	w		652		3	p			
				592		6	p			
				582		6		592	CF <sub>3</sub> def	
561	561	m	570	566		7	dp	566		
536	535	m		538		2	dp	537		
	515	vvw								
485 sh	487	w	497	489		5	p	492	NC <sub>2</sub> scissor	
	383	vw	383	378		28	p	378		
	362	vvw		365 sh			dp	364		NC <sub>2</sub> scissor or twist
	347	vw	358	352		34	dp	352		
			328	323		90	p	322		NC <sub>2</sub> wag
250	255	m	250	252		4	dp	257	CF <sub>3</sub> rock	
	248 sh	vw							CF <sub>3</sub> rock	
	232	w		237		7	dp	234	CF <sub>3</sub> rock	
	197	m		202		2	dp	202	CF <sub>3</sub> rock	
			155	153		6	p	152	CF <sub>3</sub> rock	
	116	vw		108		3	dp		N-N torsion	
				69			dp		CF <sub>3</sub> torsion	

<sup>a</sup> Abbreviations used: s, m, w, v, p, dp, sh, and str, denote strong, medium, weak, very, polarized, depolarized, shoulder, and stretch, respectively.

during this vibration resulting in a very low infrared intensity. Likewise, a large Raman intensity is expected for such a symmetric stretching motion. Appearance of the 783-cm<sup>-1</sup> band in the solid is thought to be due to a sharpening of the weak gas-phase band in accord with the usual observation. The second exception which deserves some comment is the 323-cm<sup>-1</sup> band, the second strongest Raman line. This strongly polarized line is obviously a totally symmetric vibration. However, it has no infrared counterpart, even in the solid phase. We believe this band reflects the general finding that totally symmetric vibrations often give rise to very weak infrared bands, even when the band is allowed by symmetry, and that this exception alone is not sufficient to invoke the mutual exclusion principle. The *D*<sub>2d</sub> symmetry can be ruled out on the following bases. First, the *D*<sub>2d</sub> structure requires a total of 13 Raman lines (8a<sub>1</sub> + 5b<sub>1</sub>) with no infrared counterparts whereas only one such line was found. Second, the N-N stretch would belong to the symmetry species a<sub>1</sub> and thus would be inactive in the infrared spectrum. Third, the skeletal torsional mode which appears at 116 cm<sup>-1</sup> in the infrared spectrum would be a b<sub>1</sub> mode and thus inactive. Therefore, the observed vibrational data are inconsistent with the *D*<sub>2d</sub> symmetry, and we conclude that the molecule N<sub>2</sub>(CF<sub>3</sub>)<sub>4</sub>

exists entirely in the gauche (C<sub>2</sub>) conformation in all phases.

### Vibrational Assignment

There are 48 fundamental vibrations for N<sub>2</sub>(CF<sub>3</sub>)<sub>4</sub> and 36 of these are motions of the CF<sub>3</sub> groups. The remaining 12 skeletal motions are represented by 7A + 5B. The 12 stretching vibrations (6A + 6B) of the CF<sub>3</sub> groups are expected to occur between 1150 and 1350 cm<sup>-1</sup>. The CF<sub>3</sub> stretching modes were observed to be extremely intense in the infrared spectrum and rather weak in the Raman spectrum. The only sharp Raman band in this region occurs at 1239 cm<sup>-1</sup>, and it is strongly polarized. This band is assigned to the in-phase symmetric stretch of the four CF<sub>3</sub> groups. The other bands in this region are badly overlapped with varying degrees of depolarization, and an exact assignment is not possible. However, they may be reasonably assigned to the remaining CF<sub>3</sub> stretching vibrations.

Two strong infrared bands appearing at 987 and 886 cm<sup>-1</sup> have very weak, depolarized Raman counterparts. These frequencies occur in the region where one expects to find C-N stretching motions and, on the basis of the relative intensity considerations, the bands are assigned as the two antisymmetric NC<sub>2</sub> stretching mo-

tions. The very weak, polarized Raman bands at 864 and 832  $\text{cm}^{-1}$  might be considered as candidates for the two  $\text{NC}_2$  symmetric stretches; however, the bands are extremely weak for stretching motions. Therefore, the exact assignment of the  $\text{NC}_2$  symmetric vibrations is somewhat tenuous. It is interesting to note that in the phosphorus analog  $\text{P}_2(\text{CF}_3)_4$ , the  $\text{PC}_2$  symmetric stretch is among the strongest Raman bands.<sup>18</sup>

The most intense band in the Raman spectrum occurs at 786  $\text{cm}^{-1}$ , and is assigned to the N-N stretching vibration. The complementary nature of the infrared and Raman effects is very evident for this vibrational mode, since in the infrared spectrum only a very weak band is observed. Identification of this mode would be extremely difficult without the aid of the Raman spectrum. The N-N stretching frequency of 786  $\text{cm}^{-1}$  is higher than the corresponding mode in  $\text{N}_2\text{F}_4$  and  $\text{N}_2(\text{CH}_3)_4$  which occurs at 586 and 722  $\text{cm}^{-1}$ , respectively.<sup>2,9</sup> The short N-N bond length<sup>14</sup> of 1.40 Å in  $\text{N}_2(\text{CF}_3)_4$  compared to the more normal value of 1.45 Å in other hydrazines seems to agree well with the higher stretching frequency. Similarly the long N-N bond length of 1.49 Å for  $\text{N}_2\text{F}_4$  is consistent with the 586- $\text{cm}^{-1}$  assignment of the N-N stretching motion.

The 12 deformation modes (6A + 6B) of the  $\text{CF}_3$  groups are expected to occur between 750 and 450  $\text{cm}^{-1}$ . Weak, polarized Raman bands at 764, 752, 724, 652, 592, and 489  $\text{cm}^{-1}$  are good candidates for the six A modes. The strong infrared bands at 740, 561, and 535 are assigned as B modes. The 561- and 535- $\text{cm}^{-1}$  bands have depolarized Raman counterparts, and the 561- $\text{cm}^{-1}$  band has a very broad, irregular contour suggestive of the presence of several overlapping bands. The antisymmetric  $\text{CF}_3$  deformations are probably nearly degenerate, and they are assigned to the absorptions below 600  $\text{cm}^{-1}$ . The symmetric "umbrella" deformation modes have been shown to occur at higher frequencies,<sup>19</sup> and these vibrations are assigned to the bands above 600  $\text{cm}^{-1}$ .

In the region between 300 and 400  $\text{cm}^{-1}$ , one expects to find the  $\text{NC}_2$  wag, twist, and deformational modes. Each of these motions occurs in both symmetry species so that the representation is 3A + 3B. Two depolarized and two polarized Raman bands occur in this spectral region accounting for four of the six expected modes. The polarized Raman bands at 378 and 323  $\text{cm}^{-1}$  are assigned to the in-phase  $\text{NC}_2$  scissoring and wagging motions, respectively. The scissoring motion is derived from the  $\text{NC}_3$  antisymmetric deformation and is expected to occur at a higher frequency than the wagging mode whose motion should be compared to the symmetric deformation<sup>20</sup> [in  $\text{N}(\text{CH}_3)_3$  the antisymmetric E deformation occurs at 425  $\text{cm}^{-1}$  while the symmetric mode A mode occurs at 366  $\text{cm}^{-1}$ ]. The  $\text{NC}_2$  twisting motion is assigned to the depolarized band at 352  $\text{cm}^{-1}$ . Overlapping bands due to accidental degeneracies probably account for the absence of the other expected skeletal deformations.

In the region below 300  $\text{cm}^{-1}$ , one expects eight  $\text{CF}_3$  rocking modes (4A + 4B), the N-N torsion (A), and four  $\text{CF}_3$  torsions (2A + 2B). The B species rocking modes are assigned to infrared bands at 255, 248, 232,

and 197  $\text{cm}^{-1}$ . Each of the bands has a depolarized Raman counterpart (with the exception of the shoulder at 248  $\text{cm}^{-1}$  which has no Raman counterpart). A polarized Raman band was observed at 153  $\text{cm}^{-1}$  which is somewhat low for a  $\text{CF}_3$  rock; however, it agrees quite well with a value of 155  $\text{cm}^{-1}$  for a  $\text{CF}_3$  rock in  $\text{CF}_3\text{N}=\text{CF}_2$ .<sup>21</sup> The location of the other  $\text{CF}_3$  rocks in the A species is obscured by the problem of accidental degeneracy of the rocking motions among the four  $\text{CF}_3$  groups.

A broad band centered at 116  $\text{cm}^{-1}$  in the infrared spectrum of the solid is assigned as the N-N torsional vibration. A very weak Raman band centered at 108  $\text{cm}^{-1}$  in the liquid phase is presumably the Raman counterpart of the 116- $\text{cm}^{-1}$  infrared band. This assignment is based largely on the fact that the N-N torsion in  $\text{N}_2\text{F}_4$  occurs around 120  $\text{cm}^{-1}$ .<sup>2</sup> Also, it is expected to be the lowest vibrational mode with the exception of the  $\text{CF}_3$  torsions. A very broad shoulder on the Rayleigh line centered around 69  $\text{cm}^{-1}$  may be assigned to the  $\text{CF}_3$  torsional vibrations. However, no infrared absorption is observed in this region, and this assignment is very tentative.

### Summary and Conclusions

A comparison of the Raman spectra of  $\text{N}_2(\text{CF}_3)_4$  in the solid, liquid, and gaseous states shows no evidence for the presence of more than one isomer. Similarly, a comparison between the observed infrared and Raman frequencies shows that the rule of mutual exclusion is *not* operative and it is concluded that the  $\text{N}_2(\text{CF}_3)_4$  molecule exists in the  $C_2$  gauche conformation in all three phases. The factors which are expected to be the most important in determining the conformations of the  $\text{X}_2\text{Y}_4$  molecules are the X-X bond length and the electronegativity of Y. Previous work has shown that an increased X-X bond length favors a greater percentage of the trans form.<sup>3,5,9</sup> For example,  $\text{N}_2(\text{CH}_3)_4$  has been found to be 100% in the gauche  $C_2$  form but  $\text{P}_2(\text{CH}_3)_4$  was found<sup>3</sup> to be a 60-40% mixture of the gauche and trans isomers, respectively, whereas the  $\text{As}_2(\text{CH}_3)_4$  was found<sup>5</sup> to have a 40-60% composition of the gauche and trans isomers, respectively. These results can be rationalized on the basis of exchange forces which have very high power dependence ( $1/r^6$ ) on the X-X bond length, whereas the steric forces are expected to have relatively small power ( $1/r^2$ ) dependence on this distance. Thus, for long X-X bond lengths, the steric factors are expected to be dominant and, therefore, favor the trans isomers as has been found for these molecules.

The importance of the electronegativity factor can be demonstrated by considering the isomeric composition of the  $\text{P}_2(\text{CH}_3)_4$  (40% trans) and  $\text{P}_2\text{Cl}_4$  (95% trans) molecules.<sup>3,7</sup> Since the P-P distance is expected to be nearly the same and the methyl group is about the same size as a chlorine atom, both the steric and exchange forces should be the same for these two compounds. However, the electronegativity of the methyl group ( $\sim 2.0$ ) is considerably smaller than that of the chlorine atom (3.0). Thus it appears that the increased electronegativity of the substituent favors the trans conformer.

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In comparing the conformers of  $N_2(CF_3)_4$  with  $N_2F_4$ , the electronegativity of the  $CF_3$  group is somewhat less ( $\sim 3.2$ ) than that of the fluorine atom (4.0) which would favor the gauche conformer. In addition, the short N-N bond length of 1.40 Å in  $N_2(CF_3)_4$  relative to the N-N bond length of 1.49 Å in  $N_2F_4$  favors the gauche isomer. Thus, one can rationalize the 100% gauche conformer for  $N_2(CF_3)_4$  compared to a 47% gauche in  $N_2F_4$  on the basis of the electronegativity and the X-X bond lengths. Even though the  $CF_3$  group is

quite large and expected to lead to a large steric interaction, the exchange forces dominate in the  $N_2(CF_3)_4$  molecule because of the short N-N bond length.

**Acknowledgments.**—The authors wish to thank Professor John A. Young for donating the sample of  $N_2(CF_3)_4$ . Also, the authors wish to acknowledge the financial support given this work by the National Aeronautics and Space Administration by Grant NGR-41-002-003.

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## Stereochemistry of Octahedral Titanium(IV) Complexes. II. The Titanium Tetrachloride-Titanium Tetrafluoride-1,2-Dimethoxyethane System

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Received September 22, 1971

Low-temperature fluorine-19 magnetic resonance spectra of solutions containing titanium tetrachloride, titanium tetrafluoride, and 1,2-dimethoxyethane (DME) have shown that halogen redistribution occurs to produce all possible octahedral mixed-halide complexes containing a single cis-chelated DME. Complexes containing more than one DME were not observed. Isomer ratios were determined and compared with those previously observed for similar complexes formed in the  $TiCl_4$ - $TiF_4$ -tetrahydrofuran (THF) system. Isomers containing a minimum number of chlorine atoms oriented trans to the oxygen donor are favored in the DME system whereas isomers containing a maximum of this chlorine orientation are favored in the THF system. It is suggested that significant steric interaction between THF groups and cis-oriented chlorine atoms favors isomers with chlorine atoms oriented trans to THF. In the absence of such steric interaction, the preferred orientation is with fluorine atoms trans to the oxygen donor. This is presumably due to the enhanced  $\pi$ -bonding ability of a fluorine with this orientation. The following information was determined for each of the observed complexes at  $-60^\circ$  in excess DME:  $TiF_4 \cdot DME$ , only isomer I (Figure 2) was observed with  $\delta_{FF}$  74 ppm and  $J_{FF} = 40$  Hz;  $TiClF_3 \cdot DME$ , isomer IV with fluorine trans to DME predominated with  $\delta_{FF}$  74 ppm and  $J_{FF} = 52$  Hz, isomer III with chlorine trans to DME was present in much lower concentration with  $\delta_{FF}$  82 ppm and  $J_{FF} = 36$  Hz;  $TiCl_2F_2 \cdot DME$ , isomer VI with both fluorines trans to DME predominated, isomer X with one fluorine and one chlorine oriented trans to DME was of intermediate concentration with  $\delta_{FF}$  83 ppm and  $J_{FF} = 48$  Hz, isomer VII with both chlorines trans to DME was present in very low concentration;  $TiClF_3 \cdot DME$ , isomer XI with one fluorine and one chlorine trans to DME predominated, isomer XII with two chlorines trans to DME was present in low concentration.

### Introduction

In a previous paper,<sup>1</sup> the stereochemistry of a new series of octahedral titanium(IV) complexes was discussed. These complexes were formed by halogen exchange between titanium tetrafluoride and titanium tetrachloride in excess tetrahydrofuran to give complexes of the type  $TiCl_xF_{4-x} \cdot 2THF$ . A total of 15 distinct octahedral species could exist for this system if all possible geometric isomers were formed. Fluorine-19 nmr spectroscopy could theoretically detect 13 of these species. The  $^{19}F$  nmr spectra showed the presence of only five species. Of these the stereochemistry was ascertained for three, and certain structural limitations were suggested for the remaining two. In that paper it was suggested that fluorine and chlorine undergo a similar degree of  $\pi$  bonding to titanium, which is considerably greater than the  $\pi$ -bonding ability of a THF molecule.

In an attempt to obtain additional stereochemical information about similar complexes and to reduce the complexity of the system previously studied, a bidentate chelating agent, 1,2-dimethoxyethane (DME), has now been used in place of THF. Muettert's<sup>2</sup> and

Clark and Errington<sup>3</sup> have previously examined DME complexes of both  $TiF_4$  and  $TiCl_4$ . Only 1:1 complexes were isolated. For the  $TiCl_4 \cdot DME$  complex, the DME was shown to coordinate through both oxygens to form a cis-chelate complex.<sup>3</sup> If only cis-chelated structures are considered, the number of possible species for the  $TiCl_4$ - $TiF_4$ -DME system is reduced to nine, eight of which contain fluorine. In this paper we present our interpretation of the  $^{19}F$  nmr spectra obtained for the above system and the probable stereochemistry of the species observed.

### Experimental Section

**Reagents.**—All liquid reagents were distilled under nitrogen from suitable drying agents into flame-dried storage ampoules. Titanium tetrafluoride (Ozark-Mahoning) was used as obtained. Titanium dichloride difluoride was prepared by the direct reaction of titanium tetrachloride and titanium tetrafluoride.<sup>1,4</sup> All reagents were stored in tightly sealed containers in a drybox under nitrogen and were used as soon as possible after their purification.

**Preparation of Titanium Halide Complexes.**—The  $TiCl_4 \cdot DME$  complex was easily prepared by the combination of 1 M solutions of  $TiCl_4$  and DME in benzene at room temperature. The bright yellow precipitate instantly formed and the solution was decanted. The crystals were washed with benzene and dried under

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