Contribution from the Department of Chemistry, University of
South Carolina, Columbia, South Carolina 29208

Vibrational Spectra and Structure of Tetrakis(trifluoromethyl)diarsine in the Crystalline and Fluid States[1]

J. W. THOMPSON, J. D. WITT, and J. R. DURIG*

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The infrared spectra of solid and gaseous tetrakis(trifluoromethyl)diarsine have been recorded from 1400 to 33 cm^{-1}. The Raman spectra of the liquid and solid have also been recorded and depolarization values measured. A comparison of the frequencies for the infrared and Raman bands shows the mutual exclusion principle is operative, and it is concluded that $As_2(CF_3)_4$ exists in only the trans, C_{2h}, structure in all three physical states. Assignments of the observed frequencies to the normal vibrational modes based on depolarization values, band positions, and relative intensities are presented for the molecule in the C_{2h} configuration. As an aid in making the vibrational assignments for $As_2(CF_3)_4$, the infrared and Raman spectra of tris(trifluoromethyl)arsine, $As(CF_3)_3$, have also been recorded and the data interpreted in detail.

Introduction

In recent studies[2-9] of the symmetry of molecules of the general form X_2Y_4, it has been found that of the several possible structures, only the trans (C_{2h}) and/or gauche (C_2) structures are present when the central pair of atoms is a group Va element. This corresponds to a pyramidal arrangement of neighboring atoms and nonbonded electron pairs about the central atoms. The relative amounts of the trans or gauche isomers will depend upon the interactions of the two nonbonded electronic clouds and the steric repulsions of the substituent atoms, as well as other less important forces.[10]

Although the As-As bond probably has the longest X-X bond of the group Va elements that have been studied to date, the one substituted diarsine which has been studied has been shown[5] to have a greater predominance of the trans isomer compared to the gauche form in relation to the corresponding nitrogen and phosphorus compounds. For example, tetramethyldiarsine is approximately 60% trans in the fluid states whereas the corresponding phosphorus compound is 40% trans[3] and $N_2(CH_3)_4$ has been found to be all in the gauche form.[11] Similarly, tetrakis(trifluoromethyl)hydrazine has been shown[8] to be all in the gauche form, whereas we have shown[9] the corresponding phosphorus compound to be largely in the trans form. Thus, even though the steric factors should be less pronounced for the substituted diarsines, the trans isomer may well be the more stable.

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 C_{2h} symmetry, we felt that an investigation of $As_2(CF_3)_4$ by the vibrational technique was quite desirable. Therefore, we have examined the vibrational spectra of this molecule in the fluid and solid states in order to determine the molecular symmetry and the frequencies for the normal vibrations. Also, as an aid in determining the normal modes of $As_2(CF_3)_4$, the infrared and Raman spectra of tris(trifluoromethyl)arsine are presented, along with the assignments of the normal modes.

Experimental Section

The samples of $As_2(CF_3)_4$ used in this study were prepared by the method of Brandt, *et al.*[12] The method consists of heating gray arsenic with trifluoromethyl iodide in a stainless steel bomb at 220° for 2 days. The major products are $(CF_3)_2AsI$ and $As(CF_3)_3$. Iodobis(trifluoromethyl)arsine was then allowed to react with mercury in a glass sample tube at room temperature according to the reaction $2(CF_3)_2AsI + Hg \rightarrow (CF_3)_2AsAs(CF_3)_2 + HgI_2$. Two different samples were prepared by this method in our laboratory and both samples gave identical spectra.

The infrared spectra were recorded from 1500 to 250 cm^{-1} with a Perkin-Elmer Model 621 spectrophotometer. Atmospheric water vapor was removed from the spectrophotometer housing by flushing with dry nitrogen. In the higher wave number region, the instrument was calibrated with standard gases.[13] The low wave number region was calibrated by using atmospheric water vapor and the frequencies reported by Hall and Dowling.[14] The spectra were recorded with the gaseous sample contained in a 20-cm cell equipped with CsI windows. The spectra of the solid were obtained by condensing sample on a CsI plate maintained at −190° with boiling nitrogen. Infrared spectra of $As(CF_3)_3$ and $As_2(CF_3)_4$ are shown in Figures 1 and 2, respectively.

The Raman spectrophotometer used was a Cary Model 82 equipped with a CRL Model 53A argon ion laser source.[15] All spectra were recorded using the 5145-Å line. The spectra of the liquids at room temperature were recorded with the samples sealed in capillary tubes. The spectra of the solid samples (−120°) were obtained by using a cell which was identical in design with that reported by Miller and Harney.[16] Depolarization measurements in the liquid phase were made by using the analyzer method.[17] Representative Raman spectra of $As(CF_3)_3$ in the liquid and solid phases are shown in Figure 3 and the Raman spectrum of $As_2(CF_3)_4$ is shown in Figure 4.

The far-infrared spectra of the solid samples were recorded from 33 to 300 cm^{-1} on a Beckman IR-11 spectrophotometer. The low-temperature cell used for recording the spectra at −190° has been previously described.[18] The far-infrared spectrum of $As_2(CF_3)_4$ is shown in Figure 5.

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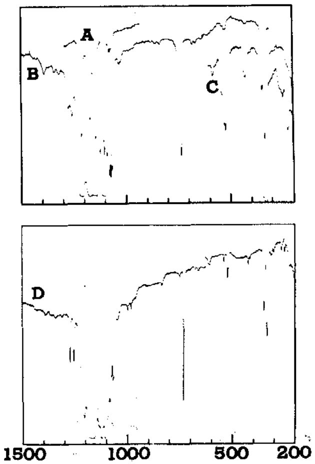

Figure 1. Midinfrared spectra of $As(CF_3)_3$: (A) gas phase at much less than 1 Torr, (B) gas phase at 1 Torr, (C) gas phase at 7 Torr, (D) solid phase at −190°. Ordinate is in arbitrary units of absorption.

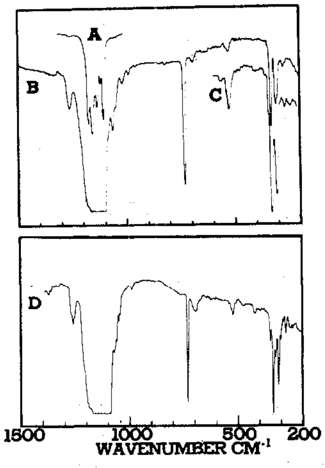

Figure 2. Midinfrared spectra of $As_2(CF_3)_4$: (A) gas phase at much less than 1 Torr, (B) gas phase at 1 Torr, (C) gas phase at 40 Torr, (D) solid phase at −190°. Ordinate is in arbitrary units of absorption.

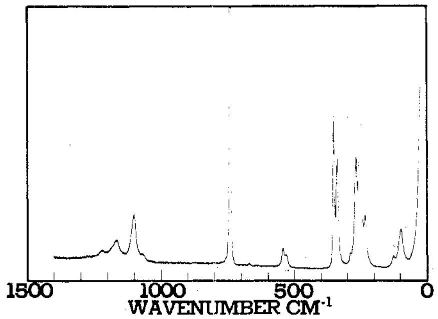

Figure 3. Raman spectrum of $As(CF_3)_3$ at room temperature. Ordinate is in arbitrary units of intensity.

Frequencies for all observed infrared and Raman bands are expected to be accurate to ±2 cm^{-1}. These frequencies are listed in Tables I and II with their relative intensities and proposed assignments.

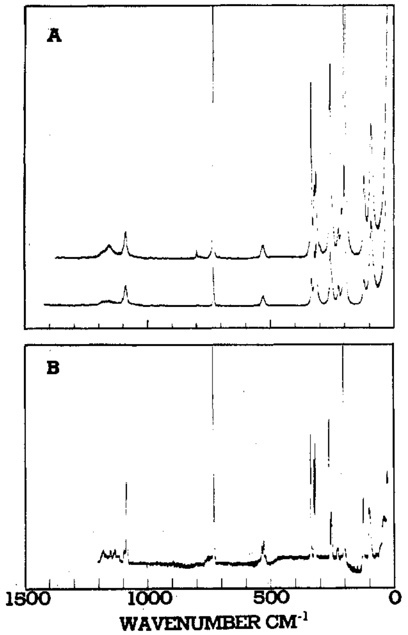

Figure 4. Raman spectra of $As_2(CF_3)_4$: (A) liquid-phase spectrum recorded at room temperature, the upper trace representing parallel polarization and the lower trace representing perpendicular polarization; (B) solid-phase spectrum recorded at −130°. Ordinate is in arbitrary units of intensity.

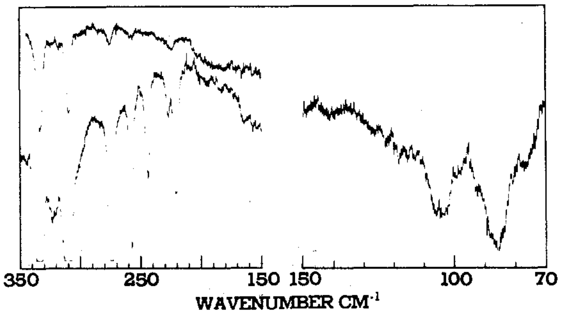

Figure 5. Far-infrared spectrum of solid $As_2(CF_3)_4$ at various thicknesses at −190°. Ordinate is in arbitrary units of absorption.

Vibrational Assignment

As an aid in making the vibrational assignment for $(CF_3)_2AsAs(CF_3)_2$, the infrared and Raman spectra of $As(CF_3)_3$ have been recorded. An analysis of the vibrational spectrum of this molecule is expected to be of considerable importance in assigning group frequencies of the As–CF_3 linkage. Therefore, the vibrational analysis of $As(CF_3)_3$ (see Table III for a summary of these assignments) will be presented first in order to put our later assignments of $(CF_3)_2AsAs(CF_3)_2$ on firmer ground.

A. $As(CF_3)_3$. Assuming C_{3v} symmetry, the 33 fundamental vibrations of $As(CF_3)_3$ are represented by 7 a_1 + 4 a_2 + 11 e. The vibrations of a_1 and e symmetry are allowed in both the infrared and Raman spectra with polarized Raman bands expected for the a_1 vibrations. The a_2 vibrations are not allowed in either the infrared or the Raman spectrum. Of the 33 fundamental vibrations, 27 are due to motions of the three CF_3 groups. The remaining six skeletal motions belong to representations of 2 a_1 + 2 e.

The trifluoromethyl group, CF_3, has a set of fairly well-defined group frequencies associated with it. As a result of accidental degeneracies caused by the presence of three CF_3 groups, only some general assignments of the CF_3 vibrations will be attempted. The highest frequency fundamental vibration of the CF_3 group is the CF_3 stretch which occurs between 1050 and 1225 cm^{-1}. These vibrational motions were observed to give rise to extremely intense infrared absorption and rather weak Raman scattering. The only strong Raman band in this region occurs at 1097 cm^{-1}, and it is depolarized. The bands due to the CF_3 stretching modes are badly overlapped with varying degrees of depolarization, so a detailed interpretation will not be attempted.

The CF_3 symmetric deformations (a_1 + e) give rise to very

Table I. Infrared and Raman Spectra of $As(CF_3)_3$ [a]

Infrared, ν, cm^{-1}		Raman			
Gas	Solid	$\Delta\nu$(liquid), cm^{-1}	Rel intens	Depolarizn	Assignment
	1272 w				540 + 733 = 1273
	1255 w				523 + 733 = 1256
1215	1204 vs	1215	2	dp	ν_1-ν_2, ν_8, ν_{12}-ν_{14}, CF_3 str
1184					
1175	1168 vs	1163	10	dp	
1149	1157 vs				
1111	1122 vs				
1107	1104 vs				
	1081	1097	17	dp	
1073	1065 m				337 + 735 = 1072
		736	90	p	ν_3, CF_3 sym def (in phase)
735	733 s				ν_{15}, CF_3 sym def (out of phase)
537	540 m	538	9	dp	ν_4, ν_{16}, CF_3 antisym def
525	523 m	525	sh		ν_{17}, CF_3 antisym def
427	423 w				334 + 99 = 433
349	349 s	348	34	p	ν_5, AsC_3 sym str
337	334 s	334	30	dp	ν_{18}, AsC_3 antisym str
	265 w	264	33	dp	ν_{19}, CF_3 rock (out of phase)
	248 w	249	100	p	ν_6, CF_3 rock (in phase)
	229 w	230	14	dp	ν_{20}, CF_3 rock (out of phase)
	127 w	125	2	p	ν_7, AC_3 sym def
	99 vw	95	12	dp	ν_{21}, AC_3 antisym def

[a] Abbreviations used in this table: vw, very weak; w, weak; m, medium; s, strong; vs, very strong; sh, shoulder; p, polarized; dp, depolarized.

Table II. Infrared and Raman Spectra of $(CF_3)_2AsAs(CF_3)_2$

Infrared, ν, cm^{-1}		Raman				
Gas	Solid	$\Delta\nu$(liquid), cm^{-1}	Rel intens	Depolarizn	$\Delta\nu$(solid), cm^{-1}	Assignment
					1183	CF_3 str
1173						
1157						
					1154	
					1137	
1134						
1119						
1105						
					1098	
		1089	6	dp	1087	
		733	98	p	732	CF_3 sym def
731	729 s					CF_3 sym def
					537	
		533	4	p	530	
536	527 m					CF_3 antisym def
527	521 m					
	348 w					246 + 105 = 351
		336	32	p	337	AsC_2 sym str (a_g)
332	335 s					AsC_2 antisym str (b_u)
	326 sh					246 + 86 = 332
		322	16	dp	324	AsC_2 antisym str (b_g)
		318	18	p	317	203 + 124 = 327
310	313 s					AsC_2 sym str (a_u)
301						
277	277 w					CF_3 rock
		258	37	p	261	
	257 w					
		253	sh		253	
	246 w					
		226	4	dp	229	
	227 sh					
	222 w					
		202	100	p	203	As–As str
		128	12	p	124	AsC_2 wag
	105 w					AsC_2 wag and twist
		98	22	wp	99	AsC_2 sym def and twist
	86 w					AsC_2 antisym def

intense infrared and Raman bands which are approximately degenerate. The in-phase component, ν_3, occurs at 736 cm^{-1} in the Raman spectrum, whereas the doubly degenerate component, ν_{15}, occurs at 735 cm^{-1} in the infrared spectrum. The CF_3 antisymmetric deformations appear in the infrared spectrum as bands of medium intensity at 537 and 525 cm^{-1} with weak Raman counterparts.

The next lowest frequency fundamental of the CF_3 group is the CF_3 rock (a_1 + 2 e). This motion gives rise to three Raman bands at 230 (dp), 249 (p), and 264 (dp) cm^{-1}. The

Table III. Summary of Vibrational Assignments for $As(CF_3)_3$ (ν_i)

Species	i	Approx description	Assignment, cm^{-1}
a_1	1	CF_3 str (–)	1100–1200
[(ir, R(p)]	2	CF_3 str (+)	1100–1200
	3	CF_3 def (+)	736
	4	CF_3 def (–)	538
	5	AsC_3 str	349
	6	CF_3 rock	248
	7	AsC_3 def	127
a_2	8	CF_3 str (–)	
[inactive]	9	CF_3 def (–)	
	10	CF_3 rock (+)	
	11	CF_3 torsion	
e	12	CF_3 str (–)	1100–1200
[ir, R(dp)]	13	CF_3 str (–)	1100–1200
	14	CF_3 str (+)	1100–1200
	15	CF_3 def (+)	735
	16	CF_3 def (–)	537
	17	CF_3 def (–)	525
	18	AsC_3 str	337
	19	CF_3 rock (–)	265
	20	CF_3 rock (–)	229
	21	AsC_3 def	905
	22	CF_3 torsion	

Table IV. Summary of the Skeletal Vibrations of *trans*-$(CF_3)_2AsAs(CF_3)_2$

Species	Approx description	Raman (solid), cm^{-1}	Ir (solid), cm^{-1}
a_g	AsC_2 str	337	
	As–As str	203	
	AsC_2 wag	124	
	AsC_2 def	99	
a_u	AsC_2 str		313
	AsC_2 twist		105
	Torsion		
b_g	AsC_2 str	324	
	AsC_2 twist	99	
b_u	AsC_2 str		335
	AsC_2 wag		
	AsC_2 def		86

249-cm^{-1} band is the strongest Raman band and is assigned as ν_6, the a_1 CF_3 rock. The two depolarized bands at 230 and 264 cm^{-1} are assigned to the doubly degenerate vibrations ν_{19} and ν_{20}. No evidence was found for the CF_3 torsion, although it is expected to occur around 50 cm^{-1}.

The remaining vibrations to be assigned are the skeletal stretching and bending modes. The symmetric and antisymmetric AsC_3 stretches are assigned to Raman bands at 348 and 334 cm^{-1}, respectively. The 348-cm^{-1} band is strongly polarized, whereas the 334-cm^{-1} band is depolarized. In the methyl derivative, $As(CH_3)_3$, these same vibrations appear at 572 and 584 cm^{-1}, respectively. The lowering in frequency is due mainly to the increased mass of the CF_3 groups. The bending vibrations of the AsC_3 skeleton are expected to be the lowest frequency fundamentals. The a_1 mode is assigned to a weak, polarized Raman band at 125 cm^{-1}, whereas the e mode is assigned to a broad, depolarized band at 95 cm^{-1}. These assignments of the skeletal motions will be useful in the discussion of the vibrational motions of $(CF_3)_2AsAs(CF_3)_2$.

B. $(CF_3)_2AsAs(CF_3)_2$. There are 48 fundamental vibrations for $As_2(CF_3)_4$, and 36 of these are motions due to the CF_3 groups. There are four CF_3 groups which result in a number of accidental degeneracies as was found for the case of $As(CF_3)_3$. The remaining twelve skeletal vibrations are represented under C_{2h} symmetry by 4 a_g + 3 a_u + 2 b_g + 3 b_u. The a_g and b_g are Raman active only, with the a_g modes giving rise to polarized Raman bands.

The twelve stretching motions of the CF_3 groups give rise to extremely intense infrared absorption and rather weak Raman scattering between 1075 and 1175 cm^{-1}. The only sharp Raman band occurs at 1089 cm^{-1}, and it is depolarized.

One of the most characteristic vibrations of the CF_3–As linkage is the CF_3 symmetric deformation. In $As_2(CF_3)_4$, the in-phase (a_g) component appears as a strong, polarized Raman band at 733 cm^{-1}, whereas an out-of-phase component (a_u or b_u) appears as an intense infrared band at 731 cm^{-1}. The CF_3 antisymmetric deformations are also fairly good group frequencies appearing at 533 cm^{-1} in the Raman spectrum and 536, 527 cm^{-1} in the infrared spectrum. These assignments of the CF_3 deformations follow directly from the previous analysis of the vibrational spectrum of $As(CF_3)_3$ and are in good agreement with it.

In $As(CF_3)_3$, the CF_3 rock of a_1 species was assigned to a very strong Raman band at 249 cm^{-1}. The corresponding band in $As_2(CF_3)_4$ appears as a strong polarized Raman band at 258 cm^{-1}. A weak shoulder is also visible at 253 cm^{-1}. This band splits completely in the solid phase. Another weak depolarized Raman band at 226 cm^{-1} is also assigned as a CF_3 rock, although the combination 128 + 98 = 226 cm^{-1} could also account for this band. However, the band appears to be depolarized which would not be consistent with the expected polarized character of the combination band. Well-defined infrared bands at 277, 257, 246, and 227 cm^{-1} are also assigned to the CF_3 rocking motion (see Figure 5). No definite evidence was obtained for the CF_3 torsional vibrations, although they are expected to occur below 50 cm^{-1}.

The assignment of the twelve skeletal vibrations of $(CF_3)_2AsAs(CF_3)_2$ will now be presented. Based on the previous analysis of $As(CF_3)_3$, the arsenic–carbon stretching mode for an As–CF_3 linkage is expected to occur between 300 and 350 cm^{-1}. The AsC_2 symmetric stretch, a_g, is assigned to a sharp, polarized Raman band at 336 cm^{-1}, approximately 12 cm^{-1} lower than the corresponding vibrational mode in $As(CF_3)_3$. The AsC_2 stretch of b_g symmetry is assigned to a doublet at 322, 318 cm^{-1}. The possibility of a combination band between two strong Raman bands at 202 + 128 = 330 cm^{-1} is thought to result in the extra band in this region. Since the combination band should be polarized, it is assigned to the 318-cm^{-1} band which is very weakly polarized. The 322-cm^{-1} band appears to be depolarized and is, therefore, assigned as the b_g fundamental. In the infrared spectrum, there are two strong bands at 335 and 313 cm^{-1} (solid-phase values). These bands are assigned as the b_u and a_u fundamentals, respectively, although the reverse assignment would be equally acceptable. Again, there are several weak bands in this region which may be accounted for by appropriate combinations of fundamental vibrations. Although there is one near coincidence of the four AsC_2 stretching modes as shown in Table IV, the general lack of coincidence in the overall spectra is taken as evidence that the principle of mutual exclusion is operative in $As_2(CF_3)_4$.

In a previous study[5] of $As_2(CH_3)_4$, the As–As stretch was assigned to a strong Raman band at 271 cm^{-1}. One normally expects the X–X stretching mode to give rise to a very strong Raman band, and it is on this basis that we assign the Raman band at 202 cm^{-1} in $As_2(CF_3)_4$ as the As–As stretch. The 202-cm^{-1} band is the strongest Raman band, and it is polarized. In addition, as seen in Figure 5, it has no infrared counterpart. This assignment is further substantiated by a comparison with the Raman spectrum of $As(CF_3)_3$. The only strong Raman band in this region occurs at 249 cm^{-1} which was assigned as due to the a_1 CF_3 rocking motion. The corresponding band in $As_2(CF_3)_4$ is at 258 cm^{-1}. The total absence of a band in the region of 200 cm^{-1} in the spectrum of $As(CF_3)_3$ is readily explained by the fact the molecule contains no As-As bond. The absence of infrared activity for this vibration provides additional evidence that the mutual exclusion principle is operative and, therefore, that the trans conformation is the correct one for $As_2(CF_3)_4$.

There are seven remaining skeletal deformations to be assigned. These assignments are facilitated by the $As(CF_3)_3$ results in which the a_1 deformation was assigned at 125 cm^{-1}, whereas the e deformation was assigned to a band at 95 cm^{-1}. Previous studies have shown[19] that the AsC_3 symmetric deformation (a_1) should be associated with an AsC_2 wagging motion and that the AsC_3 antisymmetric deformation (e) should be associated with an AsC_2 deformation. These facts are consistent with the experimental data for $As_2(CF_3)_4$. A sharp, polarized Raman band at 128 cm^{-1} is assigned as the AsC_2 wag (note that this band has almost the same frequency as the symmetric deformation in $As(CF_3)_3$). A more intense weakly polarized band at 98 cm^{-1} is considered to result from the overlapping of a polarized and depolarized band. The 98-cm^{-1} band is assigned to the remaining a_g and b_g motions, the AsC_2 deformation and twist, respectively. Again, it should be noted that this band has a counterpart in the antisymmetric AsC_3 deformation in $As(CF_3)_3$. There are three infrared-active AsC_2 bending modes, the AsC_2 wag, twist, and deformation. Of these, the AsC_2 wag was not located. The AsC_2 twist and deformation are assigned to infrared bands at 105 and 86 cm^{-1}, respectively. No evidence was found for the skeletal torsion. A summary of the assignments for the skeletal vibrations of *trans*-$(CF_3)_2AsAs(CF_3)_2$ is presented in Table IV.

Results and Discussion

A comparison of the Raman spectrum of $As_2(CF_3)_4$ in the liquid and solid phase shows no evidence for the presence of more than one isomer. Similarly, a comparison of the observed infrared and Raman frequencies shows that the rule of mutual exclusion is operative, and it is concluded that $As_2(CF_3)_4$ exists in the C_{2h}, trans, conformation in the liquid and solid phases. It was not possible to obtain the Raman spectrum of $As_2(CF_3)_4$ in the gaseous state. Therefore, the conformation in the gas phase is not determined with any certainty, although the evidence points to the trans structure.

As pointed out in previous papers,[8,9] the factors which are expected to be the most important in determining the conformations of the X_2Y_4 molecules are the X-X bond length and the electronegativity of the Y group. Previous work has shown that an increased X-X length favors a greater percentage of the trans form. Similarly, from a study of several substituted hydrazines as well as a study of $P_2(CH_3)_4$ and P_2Cl_4 it has been possible to show that a decreased electronegativity of the substituent favors the gauche isomer.

A previous study of $As_2(CH_3)_4$ showed that 60% of the molecules exist in the trans conformation with the remaining 40% presumed to be in the gauche form. Since the As-As bond length is unknown in both $As_2(CH_3)_4$ and $As_2(CF_3)_4$, a definitive statement regarding the effect of the X-X bond length is difficult to make. The As-As stretching frequency in the perfluoro compound is considerably lower than that in the methyl compound. This is at variance with the N-N and P-P stretching frequencies in which the perfluoro compound possessed both a higher X-X stretching frequency and shorter X-X bond length relative to the methyl compounds. Since the As-As stretching frequency in the perfluoro molecule is lower than the corresponding methyl compound, a longer As-As bond length is implied. This would result in a greater percentage of the trans isomer which is consistent with our experimental findings. Determination of the As-As bond length in these molecules would provide important additional information in understanding the effect of bond length changes on conformation. The electronegativity of the CF_3 group (~3.2) is considerably higher than the electronegativity of the methyl group (~2.0) which would also favor more trans isomer. Thus, the electronegativity and bond length both appear to favor a larger proportion of $As_2(CF_3)_4$ being in the trans conformation at ambient temperature compared to the approximately 60% trans found for $As_2(CH_3)_4$. Therefore, the fact that no gauche conformer was detected is consistent with these expectations as well as the general rules concerning the "gauche effect."[20]

Registry No. $(CF_3)_2AsAs(CF_3)_2$, 360-56-5; $As(CF_3)_3$, 432-02-0.

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