

## ORGANO-GROUP VB CHEMISTRY II. VIBRATIONAL STUDY OF SOME TERTIARY SUBSTITUTED ARYLARSINES AND ARSINE OXIDES

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### SUMMARY

The IR and Raman spectra of a series of arylarsines, (*p*-XC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>As and (*m*-XC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>As (X = Cl, F), and of the corresponding oxides, measured over the spectral range 4000 and 100 cm<sup>-1</sup>, are reported. A complete vibrational analysis is presented.

### INTRODUCTION

If they are considered as *para* disubstituted benzene derivatives, the phenyl groups of the *para* substituted phenylarsines and corresponding oxides belong to the C<sub>2v</sub> symmetry class. For this class all frequencies are permitted in the Raman and all but the *a*<sub>2</sub> frequency in the infrared. Similarly, the phenyl groups of the *meta* substituted phenylarsines and corresponding oxides are of C<sub>s</sub> symmetry, and for these compounds all frequencies are both IR and Raman active.

The assignments reported here are partly based on earlier work on disubstituted benzene derivatives<sup>1-7</sup>. To our knowledge, however, this paper is the first to deal with a complete vibrational assignment for monosubstituted aryl Group VB compounds. For reasons of simplicity and uniformity the numbering proposed by Varsanyi<sup>8</sup> for disubstituted benzene derivatives has been adopted here.

The IR and Raman frequencies of all the compounds are given both in solid and liquid state. The slight solvent shifts observed for some fundamentals are at present under study.

### VIBRATIONAL SPECTRA

In Tables 1 to 8 the IR and Raman spectra of the tertiary substituted arylarsines, and corresponding oxides, are given, together with a tentative assignment.

### EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 225 grating instrument using CsI windows for the 4000 cm<sup>-1</sup> to 200 cm<sup>-1</sup> region, all frequencies being measured with

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TABLE I VIBRATIONAL FREQUENCIES ( $\text{cm}^{-1}$ ) AND ASSIGNMENTS FOR  $(4\text{-FC}_6\text{H}_4)_3\text{As}$ 

IR Perfluorocarb./Nujol	Raman		Assignments
	$\text{CCl}_4$ soln.	Solid	
3087 vw	3169 w 3089 m		$2 \times 1586$ $\nu(\text{CH}) 20a (a_1)$ and $20b (b_2)$
3063 w 3040 vvw	3064 s 3041 m 3025 (sh)	3062 m	3062 m p $\nu(\text{CH}) 2 (a_1)$ $\nu(\text{CH}) 7b (b_2)$ ?
		2898 w	$1493 + 1392$ $1586 + 1298$
1894 m	1892 s		$975 + 937$
1762 w (br)	1762 m		$937 + 823$
1636 m	1641 s		$823 + 810$
1586 vs	1585 s <sup>a</sup>	1591 s	$\nu(\text{CC}) 8a (a_1)$ and $8b (b_2)$ $823 + 704$
1527 (sh)			
1493 vs	1484 vs	1490 w	1497 w p $\nu(\text{CC}) 19a (a_1)$
1449 w	1448 m		$1013 + 430$
1392 m	1391 s	1392 w	$\nu(\text{CC}) 19b (b_2)$
1335 m	1330 w		$823 + 512$
1298 s	1299 s		$\nu(\text{CC}) 14 (b_2)$
1270 m	1267 m <sup>a</sup>	1275 w	$\beta(\text{CH}) 3 (b_2)$
1231 vs	1231 vs <sup>a</sup>	1218 m	1235 m p $\nu(\text{CF}) 13 (a_1)$
1158 vs	1159 vs	1166 m	1166 m p $\beta(\text{CH}) 9a (a_1)$
1090 s	1090 s	1089 w	$\beta(\text{CH}) 18b (b_2)$
1075 m	1075 s	1072 s	1077 s p } X sens <sup>b</sup> 1 ( $a_1$ )
1066 s	1067 vs	1064 (sh)	
1024 m	1026 m	1020 w	1025 w $2 \times 512$
1013 s	1012 s	1015 w	$\beta(\text{CH}) 18a (a_1)$
957 w	954 w		$\gamma(\text{CH}) 17a (a_2)$ <sup>e</sup>
937 m	937 m		$\gamma(\text{CH}) 5 (b_1)$ $1231 - 353$
886 vw			$\gamma(\text{CH}) 17b (b_1)$
823 vs	822 vs <sup>a</sup>	824 s	828 s dp X sens <sup>b</sup> 6a ( $a_1$ )
810 s		811 vs	814 vs p $350 + 417$
762 w	763 w <sup>a</sup>		? $512 + 205$
737 w			
721 w			
704 w	703 w	704 m	704 w dp } $\phi(\text{CC}) 4 (b_1)$
696 (sh)	680 vw		
630 w	630 w	631 s	632 s dp $\alpha(\text{C}-\text{C}-\text{C}) 6b (b_2)$ $823 - 205$
615 vw	615 w		
586 s	586 s	587 m	588 m p X sens <sup>b</sup> 12 ( $a_1$ ) $205 + 353$
565 w	565 w		$823 - 277$
551 w	551 w		$\phi(\text{CC}) 16b (b_1)$
512 vs	513 vs	511 w	505 w dp $\beta(\text{CF}) 9b (b_2)$
421 s	430 s	433 w	$\phi(\text{CC}) 16a (a_2)$ <sup>f</sup>
	417 (sh)	413 vw	Phenyl-As-phenyl stretching $7a^d$
353 s	350 s	361 m	358 m dp } X sens 10b ( $b_1$ )
277 m	278 s	347 (sh)	281 m } Phenyl-As-phenyl bending <sup>d</sup>
		280 m	
		205 vs	207 vs p }
		182 w	

<sup>a</sup> Molten. <sup>b</sup> Radial skeletal vibration. <sup>c</sup> Forbidden. <sup>d</sup>  $C_{3v}$  symmetry of  $\text{AsX}_3$ . Local ( $a_1$  and  $e$ ).

TABLE 2

VIBRATIONAL FREQUENCIES ( $\text{cm}^{-1}$ ) AND ASSIGNMENTS FOR  $(4\text{-ClC}_6\text{H}_4)_3\text{As}$ 

IR		Raman		Assignments
Perfluorocarb./Nujol	$\text{CCl}_4$ soln.	Solid	$\text{CHCl}_3$ soln.	
3066 w (br)	3115 vw 3074 m 3057 (sh)	3047 m	3052 w p	$2 \times 1561$ $\nu(\text{CH}) 20b (b_2)$ $\nu(\text{CH}) 2 (a_1)$ and 13 ( $a_1$ )
	3043 (sh) 3022 w	3039 w 2897 w	3040 vw dp	$\nu(\text{CH}) 7b (b_2)$ 1478 + 1561 1577 + 1299
1898 w	1902 m			962 + 945
1785 w (br)	1788 w			821 + 945
1636 w	1643 m			821 + 813
1577 m	1576 s <sup>a</sup>	1576 m	1582 m p	$\nu(\text{CC}) 8a (a_1)$
1561 m	1559 m <sup>a</sup>		1567 w dp	$\nu(\text{CC}) 8b (b_2)$
1478 s	1479 vs			$\nu(\text{CC}) 19a (a_1)$
1435 w	1436 m			1013 + 431
1377 s	1386 vs		1384 w dp	$\nu(\text{CC}) 19b (b_2)$
1341 w	1342 w			284 + 1066
1317 vw	1323 w			821 + 507
1299 m	1299 m		1302 vw dp	$\nu(\text{CC}) 14 (b_2)$
1264 w	1250 vw <sup>a</sup>		1262 w dp	$\beta(\text{CH}) 3 (b_2)$
1206 w	1221 vw <sup>a</sup>		1211 vw	1010 + 206
1176 m	1180 m	1185 w	1179 w p	$\beta(\text{CH}) 9a (a_1)$
1092 s	1093 vs	1094 m	1096 m p	X sens 12 ( $a_1$ )
1073 (sh)	1072 (sh)			
1066 s	1065 vs	1073 vs	1074 vs p	X sens <sup>b</sup> 1 ( $a_1$ )
1063 (sh)			1069 (sh)	
1013 s	1010 s		1014 w	$\beta(\text{CH}) 18a (a_1)$
962 w	962 vw <sup>a</sup>			$\gamma(\text{CH}) 17a (a_2)^f$
945 w	943 w			$\gamma(\text{CH}) 5 (b_1)$
	903 vw			?
841 m				352 + 507
838 (sh)				
821 s	821 (sh) <sup>a</sup>			$\nu(\text{CH}) 17b (b_1)$
813 vs	810 vs <sup>a</sup>		811 w	
728 vs	726 s <sup>a</sup>	729 vs	729 vs p	X sens 6a ( $a_1$ )
717 w				$2 \times 359$
702 m	701 w <sup>a</sup>		706 w <sup>e</sup> dp	$\phi(\text{CC}) 4 (b_1)$
677 w	684 m			480 + 206
637 w	651 w	629 m	629 w dp	$\alpha(\text{C}-\text{C}) 6b (b_2)$
596 w	587 w			?
557 w	546 vw			206 + 352
509 m				
507 vs	495 vs		494 w p	X sens 20a ( $a_1$ )
497 (sh)				
480 m		474 w		$\phi(\text{C}-\text{C}) 16b (b_1)$
	431 m			1478 - 1066
359 m				Phenyl-As-phenyl
352 m	358 m	355 w		stretching <sup>d</sup>
332 m		334 m	336 w <sup>e</sup> p	

(Table continued)

TABLE 2 (continued)

IR		Raman		Assignments
Perfluorocarb./Nujol	CCl <sub>4</sub> soln.	Solid	CHCl <sub>3</sub> soln.	
318 w		322 w		β(C-Cl) 9b (b <sub>2</sub> ) ?
302 w	304 (sh) 298 w	302 w	307 w dp	
284 w	288 (sh)	288 w		X sens 10b (b <sub>1</sub> )
253 m	252 m	257 w	256 m	1066- 813
		235 w	240 m	729- 494
		206 w		Phenyl-As-phenyl bending <sup>d</sup> 15
		185 w	181 m p	
		170 w		?
		132 s		?
		99 s		X sens 11 (a <sub>1</sub> )

<sup>a</sup> Molten. <sup>b</sup> Radial skeletal vibration. <sup>c</sup> Forbidden. <sup>d</sup> C<sub>3v</sub> symmetry of AsX<sub>3</sub>. Local (a<sub>1</sub> and e).

<sup>e</sup> C<sub>6</sub>H<sub>6</sub>.

TABLE 3

VIBRATIONAL FREQUENCIES (cm<sup>-1</sup>) AND ASSIGNMENTS FOR (3-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>As

IR		Raman		Assignments
Perfluorocarb./Nujol	CCl <sub>4</sub> soln.	Solid	CHCl <sub>3</sub> soln.	
3056 w	3058 s	3060 (sh)	3065 w p	ν(CH) 2.20 a 7a, 20 b
3019 (sh)	3024 (sh)	3054 m	3056 (sh) p	
		2895 w		1594+1421 1473+1421
	1935 m			2 × 967
	1864 m			895+ 967
	1791 w			2 × 895
	1769 m			1086+ 684
	1744 m			781+ 967
	1679 m			895+ 781
1594 s	1593 s <sup>a</sup>	1597 s	1598 m p	ν(CC) 8b (a')
1585 s	1583 s <sup>a</sup>			
1575 s	1574 s <sup>a</sup>	1579 w	1581 w p	ν(CC) 8a (a')
1519 w (br)	1521 w <sup>a</sup>			
1473 vs	1473 vs	1470 w	1470 w p	1000+ 521
1421 s	1421 vs			ν(CC) 19b (a')
1411 (sh)	1410 (sh)		1416 vw p	ν(CC) 19a (a')
1298 m	1299 s	1301 w	1301 w p	
1262 s	1259 s	1260 m	1267 m p	β(CH) 3 (a')
1212 vs	1209 vs	1212 m	1219 m <sup>b</sup> p	ν(CC) 14 (a')
	1182 (sh)			ν(CF) 13 (a')
1160 m	1160 s	1163 s	1163 m p	661+ 521
	1113 vw			β(CH) 9b (a')
1086 s	1087 s	1086 m	1091 w p	445+ 684
1055 w	1057 m	1063 m	1063 m p	X sens 18b (a')
1000 s	1000 s <sup>a</sup>	1002 vs	1004 vs p	β(CH) 18a (a')
	984 vw <sup>a</sup>		992 w	X sens <sup>c</sup> 12 (a')
967 w (br)	965 w (br) <sup>a</sup>			1421- 445
				γ(CH) 5 (a'')

(Table continued)

TABLE 3 (continued)

IR		Raman		Assignments
Perfluorocarb./Nujol	CCl <sub>4</sub> soln.	Solid	CHCl <sub>3</sub> soln.	
895 m	896 m	879 w	878 (sh)	$\gamma$ (CH) 17a (a'')
867 (sh)	869 (sh)	866 m	864 m	X sens 6b (a')
856 s	857 s			$\gamma$ (CH) 17b (a'')
781 vs	779 vs <sup>a</sup>	779 m		$\gamma$ (CH) 11 (a'')
684 vs	684 vs	687 w	688 w <sup>b</sup>	$\phi$ (CC) 4 (a'')
661 m	662 vs	661 s	662 vs <sup>b</sup>	X sens <sup>c</sup> 1 (a')
560 w	559 s	559 m		$\phi$ (CC) 16a (a'')
521 s	521 vs	522 s	523 s	X sens 6a (a')
445 s	445 s			$\phi$ (CC) 16b (a'')
430 m	430 vs	428 w	433 w	$\beta$ (CF) 15 (a')
309 m		314 m	314 w	
	303 (sh)			Phenyl-As-phenyl stretching <sup>d</sup>
293 m	294 s	299 (sh)		
286 m	286 vs	289 m	291 m	
		283 (sh)		
	241 w	248 s	247 vs	X sens 10a (a'')
		239 (sh)		
	222 w	218 (sh)	216 (sh)	Phenyl-As-phenyl bending <sup>d</sup>
		211 m		
		176 (sh)		
		168 (sh)		X sens 10b (a'')
		161 vs	167 vs	

<sup>a</sup> Molten. <sup>b</sup> C<sub>6</sub>H<sub>6</sub>. <sup>c</sup> Radial skeletal vibration. <sup>d</sup> C<sub>3v</sub> symmetry of AsX<sub>3</sub>. Local (a<sub>1</sub> and e).

TABLE 4

VIBRATIONAL FREQUENCIES (cm<sup>-1</sup>) AND ASSIGNMENTS FOR (3-ClC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>As

IR		Raman		Assignment
Perfluorocarb./Nujol	CCl <sub>4</sub> soln.	Solid	CHCl <sub>3</sub> soln.	
	3143 w			2 × 1573
	3067 (sh)	3062 w		v(CH) 2, 13, 20a
3053 w (br)	3054 s	3044 w	3052 w	and 20b
		3029 w		1464 + 1573
		2897 w		?
1945 w	1942 m			2 × 971
1875 w	1875 m			971 + 903
	1808 w (br)			2 × 903
	1786 w (br)			995 + 778
	1763 m			2 × 885
1682 w	1683 m			778 + 903
1573 m	1571 vs <sup>a</sup>	1572 m	1577 m	v(CC) 8b (a')
1564 s	1562 vs <sup>a</sup>	1564 m	1569 (sh)	v(CC) 8a (a')
1464 s	1464 vs		1459 vw	v(CC) 19b (a')

(Table continued)

TABLE 4 (continued)

IR		Raman		Assignment
Perfluorocarb./Nujol	CCl <sub>4</sub> soln.	Solid	CHCl <sub>3</sub> soln.	
1405 (sh)	1405 (sh)			} $\nu(\text{CC})$ 19a ( $a'$ )
1392 m	1392 vs			
1337 w	1338 w			} 358 + 995
1293 w	1295 m	1295 vw		
1255 w	1255 w <sup>a</sup>		1264 w p	} $\beta(\text{CH})$ 3 ( $a'$ )
1207 vw	1210 vw <sup>a</sup>			
1167 w	1168 m	1167 w	1169 w p	} $\nu(\text{CC})$ 14 ( $a'$ )
1121 (sh)	1123 (sh)	1127 vw		
1103 vs	1103 vs	1108 w	1110 w p	} 778 + 431
1086 s	1086 s	1089 w	1090 w p	
1067 s	1066 s	1071 w	1071 w p	} $\beta(\text{CH})$ 9b ( $a'$ )
1052 (sh)				
995 s	992 w	996 vs	996 vs p	} X sens <sup>c</sup> 1 ( $a'$ )
971 w (br)	972 vw <sup>a</sup>			
903 w	905 w			} X sens 18b ( $a'$ )
885 m	883 s			
877 m				} $\beta(\text{CH})$ 18a ( $a'$ )
778 vs	777 vs <sup>a</sup>			
752 s	752 s <sup>a</sup>	750 w	757 w	} X sens <sup>c</sup> 12 ( $a'$ )
685 s	681 s	684 w	684 w p	
651 s	651 s	648 s	654 s p	} $\gamma(\text{CH})$ 5 ( $a''$ )
532 m		532 w	534 w <sup>b</sup> p	
526 w	529 m (br)			} ?
521 w				
431 s	432 s	437 w	436 (sh)	} $\gamma(\text{CH})$ 17a ( $a''$ )
422 (sh)	422 (sh)	422 m	423 s p	
358 m	359 m (br)	354 w	361 w <sup>b</sup> p	} $\gamma(\text{CH})$ 17b ( $a''$ )
350 m				
305 m	304 m	307 w	308 w <sup>b</sup>	} $\gamma(\text{CH})$ 11 ( $a''$ )
296 m	295 m	298 w	298 m p	
267 w	265 w	267 m	268 w p	} X sens 6b ( $a'$ )
235 w	227 w	234 m	234 s p	
		214 s		} $\phi(\text{CC})$ 4 ( $a''$ )
			201 s dp	} X sens 6a ( $a'$ )
			195 w p	
		159 s		} $\phi(\text{CC})$ 16b ( $a''$ )
		144 s		
		131 s		} Phenyl-As-phenyl bending <sup>d</sup> 9a
				} ?
				} X sens 10a ( $a''$ )
				} X sens 10b ( $a''$ )

<sup>a</sup> Molten. <sup>b</sup> C<sub>6</sub>H<sub>6</sub>. <sup>c</sup> Radial skeletal vibration. <sup>d</sup> C<sub>3v</sub> symmetry of AsX<sub>3</sub>. Local ( $a_1$  and  $e$ ).

TABLE 5

VIBRATIONAL FREQUENCIES ( $\text{cm}^{-1}$ ) AND ASSIGNMENTS FOR  $(4\text{-FC}_6\text{H}_4)_3\text{AsO}$ 

IR	Raman		Assignment			
	Perfluorocarb./Nujol	CCl <sub>4</sub> soln.			Solid	CHCl <sub>3</sub> soln.
		3177 w 3090 w			2 × 1585 ν(CH) 20a ( <i>a</i> <sub>1</sub> ) and 20b ( <i>b</i> <sub>2</sub> )	
		3070 m 3039 w 1900 w 1773 w 1644 w	3065 w 3038 vw	3064 m	p	ν(CH) 2 ( <i>a</i> <sub>1</sub> ) ν(CH) 7b ( <i>b</i> <sub>2</sub> ) 1081 + 823 939 + 823 823 + 815
1585 m		1583 m		1591 m		ν(CC) 8a ( <i>a</i> <sub>1</sub> ) and 8b ( <i>b</i> <sub>2</sub> )
1492 s	1493 s		1495 w	1498 w	p	ν(CC) 19a ( <i>a</i> <sub>1</sub> )
1396 m	1397 s					ν(CC) 19b ( <i>b</i> <sub>2</sub> )
1302 w	1299 s					β(CH) 3 ( <i>b</i> <sub>2</sub> )
1223 s	1233 vs					ν(CF) 13 ( <i>a</i> <sub>1</sub> )
1157 m	1159 vs		1165 w	1167 m	p	β(CH) 9a ( <i>a</i> <sub>1</sub> )
1081 m	1083 vs		1084 m	1084 s	p	X sens <sup>b</sup> 1 ( <i>a</i> <sub>1</sub> )
	1026 w					2 × 516
1009 w	1012 vw 939 w		994 m	996 m	p	β(CH) 18a ( <i>a</i> <sub>1</sub> ) γ(CH) 5 ( <i>b</i> <sub>1</sub> )
888 (sh)	907 vs			895 m	p	} ν(As=O)
882 s			880 m			
868 (sh)						} γ(CH) 17b ( <i>b</i> <sub>1</sub> )
838 (sh)			829 m			
823 s			822 m	827 vs		
808 (sh)			815 s	816 sh		X sens <sup>b</sup> 6a ( <i>a</i> <sub>1</sub> )
723 w (br)						516 + 206
676 m	675 s			679 w <sup>a</sup>	dp	φ(CC) 4 ( <i>b</i> <sub>1</sub> )
626				630 s	dp	α(C-C-C) 6b ( <i>b</i> <sub>2</sub> )
	587 vw		589 w	589 m	p	X sens <sup>b</sup> 12 ( <i>a</i> <sub>1</sub> )
516 s	516 vs			523 w	dp	} φ(CC) 16b ( <i>b</i> <sub>1</sub> )
508 (sh)						
419 m	420 s			416 vw	dp	β(CF) 9b ( <i>b</i> <sub>2</sub> )
370 s			373 w			} Phenyl-As-phenyl stretching <sup>c</sup>
363 (sh)	369 vs		364 w	373 w <sup>a</sup>		
352 (sh)						
321 w	316 m		317 w	313 w	dp	X sens 10b ( <i>b</i> <sub>1</sub> )
300 vw						?
275 vw			273 w			?
226 vw			233 w			?
203 vw			206 m	207 vs	p	} Phenyl-As-phenyl bending <sup>c</sup>
				184 vw		

<sup>a</sup> CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> Radial skeletal vibration. <sup>c</sup> C<sub>3v</sub> symmetry of YAsX<sub>3</sub>. Local (*a*<sub>1</sub> and *e*).

TABLE 6

VIBRATIONAL FREQUENCIES ( $\text{cm}^{-1}$ ) AND ASSIGNMENTS FOR  $(4\text{-ClC}_6\text{H}_4)_3\text{AsO}$ 

IR		Raman		Assignment
Perfluorocarb./Nujol	$\text{CCl}_4$ soln.	Solid	$\text{CHCl}_3$ soln.	
	3079 vw			$\nu(\text{CH})$ 20b ( $b_2$ )
	3061 w	3059 w	3059 w p	$\nu(\text{CH})$ 2 ( $a_1$ ) and 13 ( $a_1$ )
3036 vw		3043 w		$\nu(\text{CH})$ 7b ( $b_2$ )
3002 vw		2897 vw		1585 + 1298
	1585 vw	1579 w	1582 w p	$\nu(\text{CC})$ 8a ( $a_1$ )
1568 m	1574 w			$\nu(\text{CC})$ 8b ( $b_2$ )
1476 s	1480 s		1478 w	$\nu(\text{CC})$ 19a ( $a_1$ )
1387 s	1389 m		1375 w	$\nu(\text{CC})$ 19b ( $b_2$ )
	1364 vw			1078 + 278
1298 w	1299 vw			$\beta(\text{CH})$ 14 ( $b_2$ )
1176 w	1178 w		1186 w p	$\beta(\text{CH})$ 9a ( $a_1$ )
1093 (sh)	1096 m	1094 (sh)	1097 m p	X sens 12 ( $a_1$ )
1078 s	1079 vs	1084 s	1081 vs p	X sens 1 ( $a_1$ )
1008 s	1015 s			$\beta(\text{CH})$ 18a ( $a_1$ )
948 vw	945 vw		954 vw	$\gamma(\text{CH})$ 5 ( $b_1$ )
895 s	909 s			$\nu(\text{As}=\text{O})$ 361 + 495
887 vs		888 s	890 m p	
841 m				$\gamma(\text{CH})$ 17b ( $b_1$ )
832 (sh)				
829 (sh)				X sens 6a ( $a_1$ )
821 (sh)				
817 s			810 m p	$\phi(\text{CC})$ 4 ( $b_1$ )
737 s		730 vs	734 vs p	
700 m				$\alpha(\text{C}-\text{C}-\text{C})$ 6b ( $b_2$ )
623 w		630 m	629 m p	
502 m (sh)	503 s		507 w p	X sens 20a ( $a_1$ )
495 s				
482 m			480 vw dp	$\phi(\text{CC})$ 16b ( $b_1$ )
368 (sh)				
361 s	360 vs		370 m p	Phenyl-As-phenyl stretching <sup>a</sup> 7a ( $a_1$ )
346 (sh)				
342 m		324 m	324 m dp	$\beta(\text{C}-\text{Cl})$ 9b ( $b_2$ )
334 w				
278 w	276 w	280 vw		X sens 10b ( $b_1$ )
260 w				
		242 w	244 w	734 - 507
		209 w	209 w	
		181 m	183 s p	Phenyl-As-phenyl bending <sup>a</sup> 15
		135 m		
				?

<sup>a</sup>  $C_{3v}$  symmetry of  $\text{YAsX}_3$ . Local ( $a_1$  and  $e$ ).



TABLE 7

VIBRATIONAL FREQUENCIES ( $\text{cm}^{-1}$ ) AND ASSIGNMENTS FOR  $(3\text{-FC}_6\text{H}_4)_3\text{AsO}$ 

IR		Raman		Assignment	
Perfluorocarb./Nujol	$\text{CCl}_4$ soln.	Solid	$\text{CHCl}_3$ soln.		
3048 w	3059 w	3068 w	3068 w	p	} $\nu(\text{CH})$ 2, 20a, 7a and 20b 1583 + 1312
3008 vw		2896 vw			
	1934 w (br)				? ?
	1868 w (br)				
1594 m	1596 m	1599 m	1599 m	p	$\nu(\text{CC})$ 8b ( $a'$ )
1583 s	1588 s	1582 w			$\nu(\text{CC})$ 8a ( $a'$ )
1517 w	1518 w		1520 w		518 + 996
1473 s	1473 s		1473 w	p	$\nu(\text{CC})$ 19b ( $a'$ )
1424 s	1427 s		1414 w	p	$\nu(\text{CC})$ 19a ( $a'$ )
1312 m	1303 w				$\beta(\text{CH})$ 3 ( $a'$ )
1272 m					} $\nu(\text{CC})$ 14 ( $a'$ )
1264 m	1268 m	1274 w	1273 w	p	
1215 vs	1221 s	1222 m	1224 m	p	$\nu(\text{CF})$ 13 ( $a'$ )
1166 w		1168 w			} $\beta(\text{CH})$ 9b ( $a'$ )
1157 w	1160 w	1161 m	1161 m	p	
1084 s	1088 m	1092 w	1094 w	p	X sens 18b ( $a'$ )
1055 m	1063 w	1065 m	1065 m	p	$\beta(\text{CH})$ 18a ( $a'$ )
996 m	997 w	1004 vs	1004 vs	p	X sens <sup>b</sup> 12 ( $a'$ )
970 w (br)					1424 - 443
898 vs	870 m	904 s	904 vs	p	$\nu(\text{As}=\text{O})$
	863 (sh)				X sens 6b ( $a'$ )
859 s			857 m	dp	$\nu(\text{CH})$ 17b ( $a''$ )
788 s		794 w	791 w	dp	$\gamma(\text{CH})$ 11 ( $a''$ )
732 w (br)					1594 - 859
683 vs	681 s				$\phi(\text{CC})$ 4 ( $a''$ )
666 m	669 m	667 s	668 <sup>a</sup> m	p	X sens <sup>b</sup> 1 ( $a'$ )
557 m	560 w	562 w	557 w	dp	$\phi(\text{CC})$ 16a ( $a''$ )
518 s	521 m	519 s	524 s	p	X sens 6a ( $a'$ )
443 s	445 s				$\phi(\text{CC})$ 16b ( $a''$ )
427 m	433 w	430 w	421 w	p	$\beta(\text{CF})$ 15 ( $a'$ )
342 s	342 s				} Phenyl-As-phenyl stretching <sup>c</sup>
335 s	331 s		337 w	p	
306 w		315 w	310 s	p	
297 w	293 w		302 w <sup>a</sup>	dp	
258 w	254 w	245 s	245 m <sup>a</sup>	dp	X sens 10a ( $a''$ )
237 w	242 w	234 (sh)			} Phenyl-As-phenyl bending <sup>c</sup> 9a
		217 m	220 m	p	
		183 w			?
		146 m	160 s	dp	} X sens 10b ( $a''$ )
			154 (sh)		

<sup>a</sup>  $\text{CH}_2\text{Cl}_2$ . <sup>b</sup> Radial skeletal vibration. <sup>c</sup>  $C_{3v}$  symmetry of  $\text{YAsX}_3$ . Local ( $a_1$  and  $e$ ).

TABLE 8

VIBRATIONAL FREQUENCIES ( $\text{cm}^{-1}$ ) AND ASSIGNMENTS FOR  $(3\text{-ClC}_6\text{H}_4)_3\text{AsO}$ 

IR	Raman		Assignment	
	Perfluorocarb./Nujol	$\text{CCl}_4$ soln.	Solid	$\text{CHCl}_3$ soln.
3050 vw	3075 (sh) 3057 m 3022 vw	3061 m	3059 m	p } $\nu(\text{CH})$ 2, 13, 20a and 20b 1464 + 1563 ?
1572 m	1575 m	2897 w	1580 m	p } $\nu(\text{CC})$ 8b ( $a'$ )
1563 m	1568 m	1578 m	1571 w	p } $\nu(\text{CC})$ 8a ( $a'$ ) 683 + 787
1464 s	1480 vw 1465 s 1437 vw			$\nu(\text{CC})$ 19b ( $a'$ ) 655 + 787
1402 m	1399 s			$\nu(\text{CC})$ 19a ( $a'$ )
1307 w	1298 w			$\nu(\text{CC})$ 14 ( $a'$ )
1262 vw			1172 w	$\beta(\text{CH})$ 3 ( $a'$ )
1170 w				$\beta(\text{CH})$ 9b ( $a'$ )
1127 (sh)	1123 (sh)		1127 (sh)	} X sens <sup>a</sup> 1 ( $a'$ )
1111 s	1110 s		1114 w	
1083 m	1085 m		1089 w	X sens 18b ( $a'$ )
1070 m	1072 m		1074 m	$\beta(\text{CH})$ 18a ( $a''$ )
	1015 (sh)	1019 (sh)	1018 (sh)	} X sens <sup>a</sup> 12 ( $a'$ )
996 w	994 w	997 vs	997 vs	
917 w				?
906 (sh)				} $\nu(\text{As=O})$
898 vs	912 vs 882 (sh)	898 s	901 s	
787 vs				$\gamma(\text{CH})$ 17a ( $a''$ )
766 w				$\gamma(\text{CH})$ 11a ( $a''$ )
757 m				?
726 w (br)				X sens 6b ( $a'$ )
683 vs	680 vs			$2 \times 363$
655 s	658 s	656 s	658 s	p } $\phi(\text{CC})$ 4 ( $a''$ ) X sens 6a ( $a'$ )
530 s	530 m			$\phi(\text{CC})$ 16a ( $a''$ )
505 w	502 vw			$2 \times 254$
431 s	431 s	437 w		$\phi(\text{CC})$ 16b ( $a''$ )
		429 w	429 m	p } X sens 7b ( $a'$ )
368 s	369 s	372 w	370 w	p } Phenyl-As-phenyl stretching <sup>b</sup> 7a
363 s				} X sens 15 ( $a'$ ) [ $\beta(\text{C-Cl})$ ]
312 s	312 m	314 w	314 w	
		292 m	292 w	p } X sens 10a ( $a''$ )
254 m	246 m	258 m	258 w	} Phenyl-As-phenyl bending <sup>b</sup> 9a
222 w		214 m	239 m	
213 vw		209 (sh)	208 m	} ?
		196 w		
		172 w		
		149 vs	138 s	
		121 s		dp } X sens 10b ( $a''$ ) ?

<sup>a</sup> Radial skeletal vibration. <sup>b</sup>  $C_{3v}$  symmetry of  $\text{YAsX}_3$ . Local ( $a_1$  and  $e$ ).

an accuracy of  $\pm 1 \text{ cm}^{-1}$ . In the solid state the spectra were taken using perfluorocarbon in the region  $4000\text{--}1300 \text{ cm}^{-1}$  and as a nujol mull below  $1300 \text{ cm}^{-1}$ . In the liquid state,  $\text{CCl}_4$  was used as the solvent for the IR spectra, but for some regions with strong  $\text{CCl}_4$  absorption the solid samples were melted by heating between appropriate windows. Raman spectra were recorded on a Coderg PH1 spectrometer, the light source being an O.I.P. He/Ne laser with an output of 200 mW for the  $6.328 \text{ \AA}$  line. Depolarisation measurements were made by two successive recordings with the polarisation vector of the incident light turned through  $90^\circ$  by means of a half wave plate. Although  $\text{CHCl}_3$  was used as the principal solvent for the arsines and corresponding oxides over the region  $0\text{--}4000 \text{ cm}^{-1}$ , a supplementary spectrum for the region  $0\text{--}600 \text{ cm}^{-1}$  was also taken using  $\text{C}_6\text{H}_6$  and  $\text{CH}_2\text{Cl}_2$  as solvents for these respective compounds.

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