# CONFORMATIONS AND VIBRATIONAL SPECTRA OF 2-CHLORO-3-FLUORO-1-PROPENE AND 2-BROMO-3-FLUORO-1-PROPENE

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## ABSTRACT

The infrared spectra of 2-chloro-3-fluoro- and 2-bromo-3-fluoro-1-propene as vapours and liquids were recorded in the region 4000–50 cm<sup>-1</sup>. Additional spectra of the amorphous and crystalline solids at -170 °C and of the liquids in polar and non-polar solvents were recorded between 4000 and 200 cm<sup>-1</sup>.

Raman spectra, including semi-quantitative polarization measurements of the liquids were obtained. Spectra were also recorded with the samples dissolved in polar and non-polar solvents, and unannealed as well as annealed crystalline solids were studied at -180 °C.

Approximately 14 vibrational bands present in the spectra of the liquids, solutions and the glassy solids vanished in the infrared and Raman spectra of the crystals. From various criteria it can be concluded with certainty that the more polar (*gauche*) and less polar (*cis*) conformers were present in the crystalline chloro- and bromo- compounds, respectively. From infrared and Raman band intensities it was estimated that the conformational equilibrium in chlorofluoro-propene was highly displaced towards *cis* in the vapour, with both conformers approximately equally abundant in the liquid state (30 °C). For bromofluoro-propene the equilibrium was still further displaced towards the *cis* conformer.

A striking similarity between the spectra of the two compounds was observed. The fundamental frequencies have been tentatively assigned and checked by force constant calculations. Dipole moments and relative stabilities of the conformers were estimated by a CNDO calculation.

#### INTRODUCTION

It is well known that allylic compounds substituted in the 3-position

 $(CH_2=CH CH_2X)$  exist as mixtures of *cis* and *gauche* (rather than *trans*) conformations in the vapour and liquid states. In the crystalline state, however, one single conformer is expected and *gauche* as well as *cis* conformers have been observed depending upon the substituent X.

Correspondingly, the 2,3-dihalopropenes appear in two conformations resulting from the potential barrier around the C-C bond. Although not previously established from microwave spectroscopy or by electron diffraction techniques these conformers were also supposedly *cis* and *gauche*.

We have for some time been interested in allylic compounds from a conformational viewpoint and have studied the vibrational spectra of various allylic derivatives. Recently, our results for allylisocyanate and allylisothiocyanate [1] and for 2,3-dichloro- and 2,3-dibromo-1-propene [2] were published. In the present communication our data for 2-chloro-3-fluoro-1-propene (CH<sub>2</sub>=CCl-CH<sub>2</sub>F) and 2-bromo-3-fluoro-1-propene (CH<sub>2</sub>=CBr-CH<sub>2</sub>F) (CFP and BFP, respectively) will be presented. Simultaneously, the vapour structure of CFP was studied by electron diffraction [3] and both compounds are being investigated by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy.

#### EXPERIMENTAL

The compounds were prepared from the corresponding 2,3-dichloro-1propene and 2,3-dibromo-1-propene by interchanging the chlorine (bromine) in the 3-position with fluorine [4]. Freshly distilled dichloropropene (10.2 g) was treated with 17.5 g dried KF (heated to 300 °C for 5 h) in 70 g anhydrous diethyleneglycol under reflux. The CFP formed was distilled four times (b.p. 45 °C) and the purity studied by gas chromatography and mass spectrometry. Correspondingly, BFP (b.p. 64 °C) was prepared from dibromopropene, distilled and the purity was checked. For both compounds samples purified by preparative gas chromatography had identical infrared spectra to those purified by distillation.

The infrared spectrometer, far infrared spectrometer, far infrared interferometer, Raman spectrometer, cells, cryostats and general methods of study were described in the earlier paper [1].

#### RESULTS

The infrared and Raman frequencies observed for CFP and BFP are listed in Tables 1 and 2, respectively. With higher vapour pressures and lower moments of inertia than the 2,3-dichloro- and 2,3-dibromo-1-propenes [2], CFP and BFP had better resolved vapour contours than those molecules. Infrared spectra of BFP in the vapour, liquid and crystalline states are shown in Figs. 1, 2 and 3,



Fig. 1. The infrared spectrum of 2-bromo-3-fluoro-1-propene vapour at ambient temperature; (A) 80 torr, (B) 20 torr, 10 cm path and (C) 5 torr, 5 m path.



Fig. 2. The infrared spectrum of liquid 2-bromo-3-fluoro-1-propene (40  $^{\circ}$ C), 0.05 mm cell thickness.



Fig. 3. The infrared spectrum of crystalline 2-bromo-3-fluoro-1-propene at -170 °C.



Fig. 4. The infrared spectrum of 2-chloro-3-fluoro-1-propene vapour at ambient temperature; (A) 120, (B) 10 torr, 10 cm path and (C) 5 torr, 5 m path.



Fig. 5. The Raman spectrum of liquid 2-chloro-3-fluoro-1-propene.



Fig. 6. The Raman spectrum of crystalline 2-chloro-3-fluoro-1-propene at -180 °C.

respectively. The infrared vapour spectrum of CFP is given in Fig. 4 whereas the Raman spectrum of liquid CFP is shown in Fig. 5 and the crystal spectra in Fig. 6.

## Conformational equilibria

As apparent from Figs. 1–6 and Tables 1 and 2, the number of strong infrared and Raman bands observed in the vapour and liquid states was considerably larger than expected for molecules with 9 atoms (21 fundamentals). Therefore, the spectra immediately suggested more than one conformer per molecule. This assumption was verified since the number of vibrational bands present in the vapour and liquid states was reduced in intensities in the unannealed deposits and disappeared completely in the annealed, truly crystalline solids. Moreover, the number of strong infrared and Raman bands of the crystalline solids agrees well with the 21 fundamentals expected for one conformer. Approximately 14 additional bands for each compound were observed in the spectra of the liquids. They are marked with asterisks in Tables 1 and 2 and belong to the conformer not present in the crystals. The bands appearing in the crystal spectra were attributed to one single conformer or in many cases they were characteristic for both conformers.

Microwave studies of various 3-substituted propenes [5-8] revealed the existence of a *cis* conformer ( $C_s$  symmetry) and enanthiomorphic *gauche* conformers ( $C_1$  symmetry). We would expect similar conformations for the 2,3-dihalopropenes, in particular any *trans* conformers with  $C_s$  symmetry and eclipsed C-X bonds could be excluded. Results from the electron diffraction study [3] did indeed reveal that CFP exists predominantly in a *cis* conformation (ca. 85 % *cis*, 15 % *gauche*) in the vapour at -40 °C.

There was a striking similarity between the infrared and Raman spectra of CFP with those of BFP. Moreover, it was immediately apparent from the spectra that when an infrared band present in the vapour and liquid state of CFP vanished in the crystal spectra, then the corresponding infrared band of BFP remained in that crystal. There were some exceptions to this rule (corresponding bands of CFP and BFP both remaining in the crystal spectra) explained as bands common to both conformers. We can therefore conclude with certainty that CFP and BFP crystallized in different conformations.

The next question would be, which compound crystallized in *cis* and which in the *gauche* conformer? As recently discussed for the corresponding dichloroand dibromopropenes [2] various tests can be employed. Particularly, studies of the conformational equilibrium as a function of the dielectric constant of the molecular surroundings offer a reliable criterion. The dipole moments of these molecules will be mainly determined by the C-X bond moments, giving high dipole moments for *gauche* and very low values for *cis*. More quantitatively, this was verified by CNDO calculations on CFP (see below). Therefore, the well known stabilization of polar conformers in polar environments will give enhanced

# VIBRATIONAL SPECTRAL DATA FOR 2-CHLORO-3-FLUORO-1-PROPENE

Infrareda			Raman <sup>3</sup>		Interpretation
Vapour	Liquid	Solid <sup>e</sup> (—170°)	Liquid	Solid <sup>c</sup> (180°)	
3126 vw <sup>d</sup> )					
3119 vw $A/B$	3120 vw	3122 w	3120 s P	3125 s	v <sub>1</sub>
3111 vw )				3112 vw	
				3081 vw	
3066 vw c	a. 3050 vw		3062 w, sh	3055 s	$v_2$ gauche
			3039 s d P	е *	$v_2$ cis a'
			3015 s i P	3020 s)	v <sub>a</sub> aauche
			5015 5 1 1	3010 sj	, 3 ganone
	2995 vw		2997 s d D	*	$v_3$ cis a"
2974 m, sh	2978 m, sh		2974 w i	2973 vs	v <sub>4</sub> gauche
2959 s					
2956 s A/B	2951 m, d	*	2951 vs P	*	v₄ cis a'
2951 m <sup>J</sup>					
2944 m				2929 w	
2932 w, sn)				2904 w	
2905 m				2899 w	
2905 m)					
2899 m A/B	2890 m	2888 m	2893 m P	2892 w	$2 r_6 = 2928$
2893 m)					
2803 vw)					
2754 vw A/B	2756 vw		2755 w		
2738 vw					
1814 w	1817 w				
1797 w) 4/B					
1785 w					
1738 vw	1715 vw				
1675 s	1660 s d	*	1662 m d P	*	v5 ? cis a'
1657 s	1640 vs d		1640 s i P		comb? cis A'
1654 vs A/B	1635 vs i	* 1634 s	1635 s d P	1636 s	v5 gauche
1650 s				1618 vw	•••
1641 vs/					
1595 w)					
1583 w)					
		1510 vw		1518 VW	
1472 W	1459	1452	1462 - D	14/0 W	<u> </u>
$\begin{array}{c} 1464 \text{ m} \\ 1450 \text{ m} \end{array}$	1438 M	1433 W	1402 S P	1430 11	r6
1439 W /		1471	1122 4	T440 W /	
1420 w. ch.		1431 W, SN	1433 W U		
1425 m	1473		1425 m d D		v- cis a'
1413 m	1423 W	*	1425 W U F	* .	- /
1399 m					
1395 m					
1390 m	1390 s	1395 w	1393 m i P	1399 vs	r <sub>7</sub> gaucne
1383 m					

Infrared <sup>a</sup>			Raman <sup>a</sup>	Raman <sup>a</sup>		
Vapour	Liquid	Solid <sup>c</sup> (—170°)	Liquid	Solid <sup>c</sup> (—180°)		
1375 w) 1368 w)	1371 w, sh	1364 w	1368 m P	1367 w, sh 1362 m 1356 w, sh	v <sub>8</sub>	
$\begin{array}{c} 1307 \text{ vw} \\ 1204 \text{ vw} \end{array} A/B$	1288 w	1295 w	1295 vw		2 v <sub>16</sub> gauche	
1234 VWJ		1276 w				
1257 w 1248 w	1248 m	1245 m	1250 m P	1249 s	vg	
			1244 w, sh	1243 w, sh 1236 w, sh		
$\begin{array}{c} 1201 \text{ s} \\ 1188 \text{ s} \end{array} B$	1187 s	1184 s	1188 vw	1187 w	v <sub>10</sub> gauche	
$ \begin{array}{c} 1181 \text{ m} \\ 1175 \text{ m} \\ 1167 \text{ m} \end{array} \right) A/B \\ 1167 \text{ m} \end{array} $	1173 m	1164 w) 1158 w)	1172 vw	*	v <sub>10</sub> cis	
1158  w 1155  w $A/B1151  w$	1144 w	*	1147 vw i?	*	v <sub>11</sub> cis	
1077 w	1063 w, sh	1051	1134 vw 1074 vw	1127 w	v <sub>11</sub> gauche	
1063 s ) // n	1076 1	1051 W	1026 d D		a aia a'	
1060 vs) $A/B$	1036 vs d	*	1036 w a P	*	$v_{13}$ cis a	
1050 vs A/B	1022 vs i	1014 m	1024 w P	1015 w) 1008 w)	v <sub>12</sub>	
1023 m						
1006 s <i>C</i>	996 s i	990 m 986 s 981 s	999 m i P	996 s 984 m 981 s	v <sub>13</sub> gauche	
970 vw		968 m 961 w				
939 w. shi		949 w, sh 943 m		946 vw		
935 m $C$	926 s i	931 s 928 s 925 s	930 s i P	931 s	v <sub>14</sub> gauche	
010 c >		920 m, sh				
905 vs C 899 s	911 vs d	902 vs	916 w D		v <sub>14</sub> cis a''	
$ \begin{cases} 896 \text{ vs } \mathbf{Q} \\ 893 \text{ s} \end{cases} C $	894 vs d	*	898 vw d	*	v <sub>15</sub> cis a''	
889 s J	820 w	814 w, sh 804 w				
813 w) 796 w}	796 w	790 w, sh	798 w	792 vw	v <sub>14</sub> gauche	

TABLE 1 (continued)

## TABLE 1 (continued)

Infrared®			Raman <sup>2</sup>		Interpretation <sup>b</sup>
Vapour	Liquid	Solid <sup>e</sup> (—170°)	Liquid	Solid <sup>e</sup> (180°)	
		746 w		752 w	
739 s )					
735 vs $A/B$	725 s d	717 w	726 s P	719 w	v <sub>16</sub> cis a'
733 s					
726 S 7 708 m)		710 w)		<b>600</b>	
702 w (	710 w	707 w)		692 w	
670 w, sh		-			
660 s		643 s)			<u>_</u>
655 s $A$	641 s	638 s	643 s P	641 vs	$v_{16}$ gauche
650 s/		620 m			
	598 vw	598 w			
590 w) p	590 a i	579 5	587 c i P	584 vs	w aauche
584 w)	18 000	210.2	J02 S I I	564 43	F17 gunene
				518 W	
$\frac{449}{126}$ w B	442 m d	*	443 s P	*	v <sub>18</sub> cis a'
436 WJ					
410  W 412  m C	411 m d		412 w d D	•	$v_{17}$ cis a"
401 w		•		*	
	398 w	400 w, sh			
	390 w	394 w	388 s i P	395 m	$v_{18}$ gauche
389 w)		378 W		270 -	
380 w} A/B	377 m	370 s	376 m D ?	379 s	V19
312 W/ 357 m?		300 W/	345 m		
<i>337</i> m:			299 w		
256 m) p	251 m		250 w		Vac cis
242 m} <sup>. D</sup>	2J1 III	*	230 W	*	-20 013
228 vw			225 m	225 m	$v_{20}$ gauche
	100		185 w	* 122	at
119 W	128 m			123 w. sh	¥21
				93 w	

<sup>a</sup> Weak bands in the regions 4000–3200 and 2800–1500  $\text{cm}^{-1}$  are omitted.

<sup>b</sup> The bands belong to both conformers unless specified.

<sup>c</sup> Frequencies for annealed, crystalline solids.

<sup>d</sup> Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; P, polarized; D, depolarized (Raman); A, B, C, vapour contours; i, increased and d, decreased intensities in polar solvents. <sup>e</sup> Bands with an asterisk vanish in the crystalline solid spectra.

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### VIBRATIONAL SPECTRAL DATA FOR 2-BROMO-3-FLUORO-1-PROPENE

Infrared <sup>a</sup>			Raman <sup>2</sup>		Interpretation
Vapour	Liquid	Solid <sup>c</sup> (—170°)	Liquid	Solid <sup>e</sup> (—180°)	
3113 w <sup>d</sup> A	3112 w	3111 m	3112 s P 3091 m, sh	3111 s	v <sub>1</sub>
3051 w A	3057 w	*	3055 m	* 3043 w, sh	$v_2$ gauche
		3021 w	3042 m	3031 s 3006 w. sh	$v_2$ cis
		2989 w	2993 s i	*	v <sub>3</sub> gauche
$ \begin{array}{c} 2985 m \\ 2970 s \\ 2960 m \end{array} \\ C $	2967 w, sh	2969 m	2970 m	2966 s D	ν <sub>3</sub> cis a''
2954 s)	2946 s i	*	2944 s, sh		r₄ gauche
2940 sj 2919 w		2937 m	2935 vs d P	2932 vs 2911 vw	v4 cis a'
2902 m	7995 m	2979	2875 m	2880 m	$2 v_c = 2930$
2894  m A/B 2890 m	2885 m	2070 m	2075 m	2000 m	2 76 - 2750
1657 s		1655 w, sh			/
1652 s} A/B 1646 s	1649 s d	1649 s	1648 vs d P	1648 vs	$v_5 cis a_1$
1635 m, sh	1636 s i	<b>*</b> 1624 w	1635 vs i P	*	v5 gauche
1616 w 1607 w 1603 w 1600 w	1598 m	1618 w 1596 m		1596 w	
1465 m 1462 w 1459 m 1457 m	1456 s	1452 s	1454 s P	1451 vs	r <sub>6</sub>
1448 w, sh 1437 w 1430 w		1440 w	1447 m, sh		
	1421 w, sh	1419 w			
$ \begin{array}{c} 1413 \text{ s} \\ 1409 \text{ s} \\ 1403 \text{ s} \end{array} $	1409 s d	1412 m	1411 m, sh P	1413 s	v7 cis a'
= *			1404 m		
1390 w 1381 m	1384 s i	1395 vw) 1389 vw)	1384 m	*	$v_7$ gauche
1363 w, Q 1355 w	1362 w, sh	1361 m	1360 m P	1362 s	v <sub>8</sub>
1279 w 1274 w	1289 vw	1290 w			

# TABLE 2 (continued)

Infrared®			Raman		Interpretation <sup>b</sup>
Vapour	Liquid	Solid <sup>e</sup> (—170°)	Liquid	Solid <sup>e</sup> (—180°)	
1253 m		·······			
1249 w 1244 m 1240 m sh	1245 m	1250 w) 1233 w)	1244 m P	1238 s	ν <sub>9</sub>
1240 w, sn J	1221 w				
1191 m					,
1186 m} A/B 1180 m	1178 s i	*	1175 w		r <sub>10</sub> gauche
1151 m 1145 m	1135 m d	1178 m	1133 w	1129 s	Via CIS
1141 m 1118 w	1155 m d	1120 m	1155 ₩	1127 5	P10 C13
1108 w A/B 1097 w	1097 vw	1096 vw	1096 vw		$\nu_{11}$
1067  vw = A/B	1038 s d	1036 s	1035 w, sh	1034 w	v <sub>13</sub> cis
1049 vs)	1004	1028 vs)		1024 vs)	
1042 vs) $A/B$	1024 vs	1018 s	1022 m	1012 vs)	<i>v</i> <sub>12</sub>
1015 w, sh		1012 w, sh			
		1004 w, sh	~~~	1002 vw	in and the
1002 m C	996 s i	* 968 w	995 m	*	v <sub>13</sub> gauche
024 - C	027 sh	938 W			n anche
934  m C	<i>321</i> w, sit	* 076 c)			P14 gauene
909 vs	915 s d	909 sj	926 vs d D	923 vs	v <sub>14</sub> cis a''
$ \begin{cases} 900 \text{ vs} \\ 894 \text{ w, sh} \end{cases} C $	899 s d	900 m 896 m	904 w d D	902 vs	$v_{15}$ cis a''
858 w	858 w	070 111			
	797 w	792 w			
$ \begin{array}{c} 772 \text{ w} \\ 767 \text{ s} \end{array} \right\} C $	770 w	*			$v_{15}$ gauche
740 w					
735 w 730 w <i>A/B</i>	721 w	731 w 728 w	725 vw		
728 wJ	(00	700		700 w	
696 w, sh	699 m	692 m	694 w	700 w	
680 s 675 vs	673 s d	677 s 673 w	674 vs P	676 vs	v <sub>16</sub> cis a'
673 s J		<i></i>			
00/ m	668 w, sh	669 w, sh			
UUU W, SN	644 32	003 W			
586 m	U <del>UT</del> W	042 VW			
580 m	575 s i	*	575 w	÷.	v <sub>16</sub> gauche

Infrared <sup>a</sup>		Ramanª	Ramanª		
Vapour	Liquid	Solid <sup>c</sup> (—170°)	Liquid	Solid <sup>c</sup> (—180°)	
			545 m, sh		
$ \begin{array}{c} 552 \text{ m} \\ 547 \text{ m} \\ 540 \text{ m} \end{array} \right\} A/B $	538 s i	*	538 vs P	*	v <sub>17</sub> gauche
508 w 503 w			493 w		
499 w)	471 w				
$\begin{array}{c} 397 \text{ w} \\ 398 \text{ s} \\ 379 \text{ w} \end{array} \right\} C$	393 s i	392 s	394 w D	397 m	ν <sub>17</sub> cis a''
515		383 w			
371 w) 360 w	365 m	365 s	365 vs P	364 vs	v <sub>18</sub> cis a'
,	344 s	*	348 s P 322 vw)	*	$v_{18}$ gauche
	318 m	325 m	319 m P 309 vw	326 m	v <sub>19</sub>
$\begin{array}{c} 226 \text{ m} \\ 221 \text{ m} \end{array} B$	224 m	233 s 227 m	222 w	234 w	v <sub>20</sub> cis
203 w C	204 m	,	204 m	<b>*</b> 163 w	$v_{20}$ gauche
$ \begin{array}{c} 118 \text{ w} \\ 113 \text{ m} \\ 110 \text{ w} \\ 102 \text{ w} \end{array} \right\} C $		120 vw		120 vw, sh	$v_{21}$ hot bands
103 W J				99 w 86 vw, sh 72 w 53 vw, sh	lattice modes

TABLE 2 (continued)

<sup>a</sup> Weak bands in the regions 4000-3200 and 2800-1500 cm<sup>-1</sup> are omitted.

<sup>b</sup> The bands belong to both conformers unless specified.

<sup>e</sup> Frequencies for annealed, crystalline solids.

<sup>d</sup> For abbreviations, see footnotes to Table 1.

e Bands with an asterisk vanish in the crystalline solid spectra.

(diminished) intensities of gauche (cis) bands when changing from non-polar to polar solvents. Following our earlier notation [2], infrared and Raman bands are denoted as i or d (Tables 1 and 2) if their intensities increase or decrease, respectively, in the order  $CCl_4$  – neat liquid –  $CH_2Cl_2$ – $CH_3CN$ . It can be seen that for CFP the d bands disappeared in the crystal spectra whereas the i bands remained (Table 1) and vice versa for BFP (Table 2). Therefore, CFP crystallized in the gauche conformer like dichloro- and dibromopropene [2], whereas the crystalline BFP consisted of molecules in the cis conformation. For certain bands no intensity variations were observed, either due to incomplete data (weak band intensities, solvent bands etc.) or more important: the bands had contributions from both conformers, resulting in negligible intensity variations.

The same conclusion can be drawn from infrared band intensities of the vapours compared to the liquids in the two compounds. Thus, the vapour bands at 1654, 1395, 1194, 1006, 655 and 587 cm<sup>-1</sup> of CFP had relatively higher intensities in the liquid state. Correspondingly, in BFP the vapour bands at 1390, 1186, 1002, 580 and 547 cm<sup>-1</sup> were also enhanced in the liquid. These effects agreed with the predicted stabilization of the polar *gauche* conformer in the neat liquids.

These attributions of infrared and Raman bands to the *gauche* and *cis* conformers are in agreement with empirical group frequencies for the C=C stretching modes in other halogenated allyl compounds. It was reported for the allyl halides [9] and the 2,3-dichloro- and 2,3-dibromo propenes [2, 10, 11] that the *gauche* fundamentals were at lower frequencies than those of the *cis*. However, for allyl cyanide [12], isocyanate [1] and isothiocyanate [1] these fundamentals overlapped and for allylamine [13] the *gauche* C=C stretch was at a higher frequency than for the *cis*, suggesting precautions in applying these criteria to allylic compounds with widely different substituents.

Great care should be taken when inferring conformational abundance from infrared and Raman band intensities. However, as is apparent from Fig. 1 and Table 1, by far the most intense infrared bands in the vapour phase of CFP: 1060, 905, 896 and 735 cm<sup>-1</sup> belonged to the *cis* conformer. For BFP (Fig. 4, Table 2) the corresponding *cis* vapour bands at 1045, 909, 900 and 675 cm<sup>-1</sup> had even higher relative intensities, indicating considerable excess of the *cis* conformer in both compounds (particularly in BFP). In the liquid state, however, the *cis* and *gauche* conformers have infrared as well as Raman bands of comparable intensities, suggesting roughly equal abundance of the conformers (again probably more *cis* in BFP than in CFP).

No distinct intensity variations of the infrared or Raman bands were detected when the liquids were cooled from ambient temperature down to the freezing points, suggesting small enthalpy differences between the conformers in the liquid state. Therefore, it was not surprising that CFP and BFP crystallized in opposite conformers since intermolecular crystal forces might be the deciding factor. These compounds would be interesting candidates for high pressure crystallization at ambient temperature, sometimes (e.g. for 1,3-diiodopropane [14] and various cyclohexanes [15]) giving another conformer than the low temperature crystallization. However, with the low melting points of these compounds, no crystallization was achieved when applying pressures up to ca. 50 kbar.

### Vibrational assignments

The 21 fundamentals of the *cis* conformer will divide themselves between 14 a' and 7 a''. Employing the preliminary [3] structural parameters for CFP the

following moments of inertia were calculated:  $I_A = 57$ ,  $I_B = 216$  and  $I_C = 270$  amu. Å. With all the heavy atoms in the symmetry plane the largest moment of inertia will be perpendicular to this plane. Accordingly, the a'' fundamentals should have C-type contours with prominent Q-branches in the infrared vapour spectra. The a' contours will be hybrides between A and B, and the following PR separations were calculated [16]: A(13) B (11) and  $C(19 \text{ cm}^{-1})$ . For the slightly heavier BFP the PR separations were calculated by the same procedure giving 10, 8 and 14 cm<sup>-1</sup> for the A, B and C bands, respectively. Since the gauche conformers had no symmetry, the vibrational modes should in principle all be polarized in Raman and have A, B, C hybrid infrared vapour contours.

Vapour bands with apparent C contours were observed at 1006, 935, 905, 896 and 412 cm<sup>-1</sup> in CFP and at 1002, 934, 909, 900, 767 and 389 cm<sup>-1</sup> in BFP. However, from reasons already discussed, not all these bands belonged to the *cis* conformers as might be anticipated.

The vibrational bands tentatively assigned as fundamentals are listed in Table 3. With the *gauche* and *cis* conformers present alone in the crystalline CFP and CBP, respectively, a complete list of fundamentals for these conformers was given. The additional *cis* (*gauche*) fundamentals for CFP (BFP) were also listed in Table 3. When not specified the *gauche* (CFP) and *cis* (BFP) bands were common to both conformers. The *cis* (*gauche*) bands for CFP (BFP) can be attributed to one conformer with reasonable certainty. The *gauche* (*cis*) bands, however, might be attributed to one or to both conformers, unless the i or d (increased or decreased intensities in polar solvents) justified a specific attribution. Our main goal was to divide the bands into *gauche* and *cis* fundamentals, the assignment of the *cis* modes into *a'* and *a''* species were in some cases fairly uncertain.

The four CH stretching vibrations (asymmetric  $(v_1)$  and symmetric  $(v_2)$  vinyl CH<sub>2</sub> and asymmetric  $(v_3)$  and symmetric  $(v_4)$  methylene CH<sub>2</sub>) were observed close to the corresponding frequencies [2] in 2,3-dichloro- and 2,3-dibromopropene. The present data indicated that all the CH stretches except  $v_1$ , have separate bands for the *cis* and *gauche* conformers, whereas for the dichloro- and dibromopropene [2], the allyl halides [9] and allylcyanide [12] most of these fundamentals were common to both conformers. As apparent from Tables 1 and 2 we have interpreted the medium intense infrared vapour bands at 2899 and 2894 cm<sup>-1</sup> in CFP and BFP, respectively, as  $2v_6$  in Fermi resonance with  $v_4$ . This assignment agrees well with that of similar molecules [2, 9, 12], although these bands might eventually be interpreted as fundamentals.

Since the C=C stretching bands have been used for diagnostic purposes [10] for 2,3-dihalopropenes, the assignment of these fundamentals was of particular interest. For BFP the *cis* and *gauche* modes ( $v_5$ ) were assigned to infrared bands observed at 1649 and 1636 cm<sup>-1</sup> (liquid values), respectively, the vapour frequencies being less definite. For CFP the vapour band at 1675 cm<sup>-1</sup> disappeared in the crystal and might be  $v_5$  for the *cis* conformer. However, the vapour band with

Chlorofluoropropene			Bromoflu	oropropene		Approximate <sup>6</sup>	
Gauche	Cis		Gauche	Cis		description	
observ.	observ.	calc.°	observ.	observ.	calc.°		
3119	_	3092		3113	3092	$\nu_1$ -CH <sub>2</sub> asym str	
3066	3039ª a'	3026	3051	3042 <sup>d</sup>	3026	$v_2 = CH_2$ sym str	
3015-	2995° a''	2991	2993	2970 a''	2991	$r_3$ CH <sub>2</sub> asym str	
2974	2956 a'	2948	2950	2935ª a´	2948	$v_4 CH_2$ sym str	
1635°	1660° a''	1660	1636°	1649° a'	1654	$v_5 C \sim C \operatorname{str}$	
1464		1484	~	1465	1480	v <sub>6</sub> CH <sub>2</sub> scissor	
1395	1425 a'	1373	1386	1409	1370	$\nu_7 = CH_2$ scissor	
1371	_	1366		1363	1358	$v_8 CH_2$ wag	
1252	-	1320		1244	1319	$v_9 = CH_2$ bip	
1194	1175	1183	1186	1145	1168	$v_{10}$ CH <sub>2</sub> twist	
1077	1155	1100		1108	1100	$v_{11}$ -CH <sub>2</sub> rock	
1050		<b>9</b> 85		1045	98 <i>5</i>	$v_{12}$ C–F str	
1006	1060 a'	958	1002	1054	958	$v_{13}$ C–C str	
935	905 a''	898	934	909 a''	893	$v_{14}$ CH <sub>2</sub> rock	
804	896 <i>a''</i>	880	767	900 a''	875	$v_{15} = CH_2$ bop	
655	735 a'	751	580	675 a'	727	$v_{16}$ C-X str	
587	412 a''	658	547	389 a''	652	$v_{17}$ skel bend	
390°	442 a'	454	344	365 a'	387	$v_{18}$ skel bend	
380	_	331		318	310	r <sub>10</sub> skel bend	
225ª	249	258	203	223	244	$v_{20}$ skel bend	
119		158		113	149	$v_{21}$ torsion	

FUNDAMENTAL FREQUENCIES<sup>3</sup> FOR *cis* and *gauche* conformers in 2-chloro-3-fluoro- and 2-bromo-3-fluoro-1-propene

<sup>a</sup> The frequencies are infrared vapour values except when noted.

<sup>b</sup> Not derived from the calculations.

<sup>c</sup> For details see text. The force constants are not listed for the sake of brevity.

<sup>d</sup> Raman liquid values.

<sup>e</sup> Infrared liquid values.

a central maximum at 1654 cm<sup>-1</sup> corresponded to two close bands at 1640 and 1635 cm<sup>-1</sup> in the liquid, of which only the latter remained in the crystal and undoubtedly was  $v_5$  (gauche). The 1640 cm<sup>-1</sup> band might be the *cis* fundamental rather than 1675 cm<sup>-1</sup>, but the conflicting increase/decrease in polar solvents in infrared and Raman, respectively, and small frequency shift between the 1640 and 1635 cm<sup>-1</sup> lines left us with the assignments of Table 3.

The infrared vapour bands 1464 (CFP) and 1465 cm<sup>-1</sup> (BFP) with A contours were assigned as the  $v_6$  fundamentals involving the methylene CH<sub>2</sub> scissor close to the value given for allyl fluoride [9]. Since these bands remained in the crystalline state (with reduced intensity for CFP) they were attributed to both conformers. The bands at 1425 and 1409 cm<sup>-1</sup> (*cis*) and 1395 and 1386 cm<sup>-1</sup> (*gauche*) for CFP and BFP, respectively, are the  $v_7$  modes, involving the vinyl CH<sub>2</sub> scissor. Weak infrared vapour bands around 1370 cm<sup>-1</sup> with polarized

Raman counterparts were assigned as the  $v_8$  modes in the two compounds. Also, infrared vapour bands at 1252 (CFP) and 1244 cm<sup>-1</sup> (BFP) were attributed as  $v_9$ . The data indicated that both  $v_8$  and  $v_9$  were common to both conformers.

In BFC the well resolved A/B vapour bands at 1186 and 1145 cm<sup>-1</sup>, in spite of their similarity belonged to different conformers and were assigned as  $v_{10}$ . The contours in CFP were uncertain, but the bands at 1194 and 1175 cm<sup>-1</sup> were assigned as the *gauche* and *cis* bands of  $v_{10}$ , respectively. For both compounds the corresponding Raman bands were very weak. We would expect this mode to be of species a'' for the *cis* conformer (CH<sub>2</sub> twist), although not supported by C-type contours in the infrared vapour spectra. The weak infrared band at 1108 cm<sup>-1</sup> was tentatively interpreted as  $v_{11}$  for both conformers of BFP. For CFP the assignment of  $v_{11}$  to 1155 cm<sup>-1</sup> (*cis*) and 1077 cm<sup>-1</sup> (*gauche*) was even more uncertain.

A striking similarity between the spectra of CFP and BFP was apparent in the region 1070–850 cm<sup>-1</sup>, involving frequencies, infrared and Raman intensities, infrared vapour contours and Raman polarization data. Obviously, these features must be recognized by the actual assignments in this region. The A/B bands at 1060 (CFP) and 1054 cm<sup>-1</sup> (BFP) belonged to *cis*, the A/B bands at 1050 (CFP) and 1045 cm<sup>-1</sup> (BFP) were common to both conformers. Infrared vapour bands at 1006 (CFP) and 1002 cm<sup>-1</sup> (BFP) definitely belonged to the *gauche* and so did those at 935 (CFP) and 934 cm<sup>-1</sup> (BFP). These four bands had prominent C-type contours, suggesting a'' modes of the *cis* conformer. Thus the A, B, C hybrid contours of the *gauche* conformers evidently had nearly pure C character for these bands.

The close bands at 905 and 896 cm<sup>-1</sup> (CFP) and 909 and 900 cm<sup>-1</sup> (BFP) were all *cis* bands, and the prominent *C* contours indicated a'' fundamentals. The surprisingly close spacing between these a'' modes (9 cm<sup>-1</sup> for both compounds) was also reported for allyl cyanide [12] (12 cm<sup>-1</sup>). Very high infrared and low Raman intensities of the bands around 1050 cm<sup>-1</sup> suggested C-F stretching fundamentals, probably mixed with C-C stretching modes.

The weak infrared vapour bands at 804 cm<sup>-1</sup> in CFP and at 767 cm<sup>-1</sup> in BFP were tentatively assigned as the *gauche* bands of  $v_{15}$ . Very intense infrared vapour bands with A/B contours at 735 (CFP) and 675 cm<sup>-1</sup> (BFP) were assigned as the *cis*, the less intense ones at 655 and 580 cm<sup>-1</sup> as the *gauche* fundamentals  $v_{16}$ , mainly connected with the C-Cl(Br) stretch.

Less intense, the gauche bands at 587 (CFP) and 547 cm<sup>-1</sup> (BFP) with hybrid contours were assigned as  $v_{17}$ . The vapour bands at 412 and 389 cm<sup>-1</sup> in CFP and BFP, respectively, had distinct *C*-type contours and since they belonged to the *cis* conformers were attributed to the *a*" modes  $v_{17}$ . Bands at 442 and 390 cm<sup>-1</sup> for CFP and 365 and 344 cm<sup>-1</sup> for BFP were assigned as the *cis* and *gauche* fundamentals, respectively, of  $v_{18}$ , whereas 380 (CFP) and 318 cm<sup>-1</sup> (BFP) were presumably the overlapping *cis* and *gauche* modes  $v_{19}$ . Infrared vapour bands at 249 (CFP) and 223 cm<sup>-1</sup> (BFP) with apparent *B* contours were assigned as the *cis*, those at 225 cm<sup>-1</sup> (Raman liquid) and 203 cm<sup>-1</sup> as the *gauche* bands of  $v_{20}$ . Finally, the lowest fundamental  $v_{21}$  mainly connected with a CH<sub>2</sub>F torsional motion was attributed to the weak vapour bands at 119 (CFP) and 113 cm<sup>-1</sup> (BFP). Some additional sharp peaks in BFP might be hot band progressions. No other bands were detected in the vapour or liquid states, and separated *cis* or *gauche* fundamentals  $v_{21}$  were not confirmed. Torsional modes at 119 and 113 cm<sup>-1</sup> for CFP and BFP agree reasonably well with our new data for 1,2-difluoroethane [17]. Here infrared vapour bands were observed at 136 (*gauche*) and 152 cm<sup>-1</sup> (*trans*) and the earlier, uncertain Raman value [18] at 196 cm<sup>-1</sup> was not reproduced.

A number of weak infrared (and some Raman) bands were observed which were not assigned as fundamentals. We do not generally know to which conformer they belong. For this reason and with the low symmetry and many fundamentals of CFP and BFP, we have not considered it worthwhile to explain these lines as combination bands or overtones.

### Force constant calculations

It is our intention to make normal coordinate analyses of the 2,3-dihalopropenes in which the derived force fields will be fitted to a series of molecules. In this communication we shall only give some preliminary results used as an aid for the assignments. For this purpose reasonable diagonal stretching and more uncertain diagonal bending force constants were transferred to the *cis* conformers of CFP and BFP. More realistic frequencies were obtained after introducing seven additional stretching interaction terms. The same force constants were employed for both molecules, except that the vinyl C-X stretching term of 3.5 for Cl was reduced to 3.1 mdyn/Å for Br. Using a slight modification of the Gwinn [19] program, the normal frequencies listed in Table 3 were calculated. Considering the crudeness of the calculations the correspondence between the observed and calculated frequencies was generally satisfactory except for  $v_9$ ,  $v_{13}$  and particularly  $v_{17}$ . The observed frequency shifts for corresponding fundamentals in CFP and BFP were reasonably well reproduced.

## **CNDO** calculations

Using the simple CNDO/2 approximation [20, 21] and an *spd*-basis set, the dipole moments and conformational energies of CFP were calculated. These results are given in Table 4 together with the necessary parameters as a function of the dihedral angle between the plane defined by the vinyl group and the CCF atoms. The data demonstrated the large difference in dipole moments between the *cis* and the *gauche* (90°-120°) conformers in agreement with the observed vari-

	Dihedral angle	Energy (a.u.)	$ \Delta E \\ (kcal mol^{-1}) $	Dipole moment (D)
cis	0	68.16824	0	0.13
	30	-68.16701	0.77	0.89
	60	-68.16483	2.14	1.71
aaucha	) 90	-68.16418	2.55	2.38
yuucne	120	-68.16486	2.13	2.84
	150	-68.16536	1.81	3.08
trans	180	68.16554	1.69	3.15

CONFORMATIONAL ENERGIES AND DIPOLE MOMENTS FOR 2-CHLORO-3-FLUORO-1-PROPENE CALCULATED BY CNDO/2

ations in the conformational equilibria. The conformational energies, however, had a sharp minimum for *cis*  $(0^{\circ})$  and an additional shallow minimum for *trans*  $(180^{\circ})$  rather than *gauche*  $(90^{\circ}-120^{\circ})$ . Similar results were obtained for 2,3-di-fluoropropene, whereas 2-fluoro-3-chloro-1-propene on the other hand, displayed a distinct potential minimum at  $105^{\circ}$ . Evidently, much more refined methods of calculation would be necessary to derive the conformational energies for CFP.

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