

Studies of the Conformation of Halogenocyclohexanes in the Crystalline State

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The infrared spectra of chloro, bromo, and iodocyclohexane were recorded in the region $4000-200\text{ cm}^{-1}$ as liquids and as crystalline solids at -160° . Moreover, the compounds were crystallized at room temperature under high pressure and infrared spectra were obtained with a high pressure cell equipped with diamond windows. All the three molecules crystallize with the halogen substituent in the *e*-conformation at low temperature and at high pressure.

The infrared vapour phase spectra of chloro and bromocyclohexane were recorded, and Raman spectra of all the molecules obtained. A striking similarity between the vibrational spectra of these molecules was observed. Most of the fundamental modes for the equatorial (*e*) and the axial (*a*) conformers coincide. For chloro, bromo, and iodocyclohexane 6, 6 and 9 modes were split into an *e* and an *a* component, respectively.

More than a decade ago we studied¹ some monohalogenated cyclohexanes by spectroscopic technique. It was clear from the spectra that both the *e*- and the *a*-conformations of chloro- and bromocyclohexane were present in the liquids, the *e*-conformation predominating. In the true crystalline state, however, only the *e*-conformations were present, although chlorocyclohexane first solidifies into a cubic modification containing both conformations,¹ before the anisotropic crystal is reached at lower temperatures.

The conformational equilibrium of cyclohexane derivatives in the liquid has been extensively studied in recent years, particularly by proton magnetic resonance technique, and is reviewed in two monographs.^{2,3} However, very few investigations have been concerned with these molecules in the crystalline state and the conditions deciding which of the two conformers that are present. This can most accurately be done by X-ray methods at lower temperatures, but vibrational spectroscopic methods are also well suited for such studies. Particularly, by applying a high pressure cell with windows transparent for infrared radiation,⁴ the high-pressure crystal can conveniently be studied. It was reported by Brasch⁵ that in halogenated ethanes, the low temperature and the high pressure crystals can consist of molecules in different conforma-

tional forms. We felt it would be of interest to extend such studies to the cyclohexanes. In the present paper the low temperature and the high pressure crystalline spectra of chloro, bromo, and iodocyclohexane have been compared. Although we have previously reported the infrared and Raman spectra of chloro and bromocyclohexane, the modern infrared grating spectrometers have a much better resolution and wider spectral range and these data have therefore been repeated. In addition, spectra of the vapours were obtained using a ten meter path length cell. By means of helium-neon laser excitation better Raman spectra were obtained for chloro- and bromocyclohexane. Since iodocyclohexane decomposes in mercury light,⁶ only incomplete Raman spectra have previously been recorded. A quite satisfactory Raman spectrum was obtained with laser excitation and semiquantitative polarization data were calculated.

EXPERIMENTAL

Chemicals. Chloro-, bromo-, and iodocyclohexane were all commercial products from Baker, which were purified by two times fractionation in a rotaband column. The purity was checked by gas chromatography.

Instrumental. The infrared spectra were recorded in the region $5000-200\text{ cm}^{-1}$ with a Perkin-Elmer model 225 spectrometer. A Beckman 10 m gas cell was employed for the vapours, but no vapour spectrum was obtained for the iodine compound. The liquids were filled in sealed cells with potassium bromide and polyethylene windows and the crystals were studied in a low temperature cell from RIIC, using dry ice and liquid nitrogen as refrigerants. For the high pressure experiments, a cell with type II diamonds⁴ was used in connection with a Perkin-Elmer model 621 spectrometer, equipped with a $6\times$ beam condenser. Spacers of molybdenum or stainless steel were used between the diamonds, and the samples situated in a hole of approximately 0.3 mm diameter. The technique for obtaining polycrystalline as well as single crystals with the diamond cell was described by Brasch.⁷ Due to the very small sample size, the high pressure infrared spectra were recorded at the expense of high resolution, using wide slits, high gain and slow recording speed. Fairly satisfactory spectra were obtained in the spectral region $1600-450\text{ cm}^{-1}$.

Raman spectra were recorded with the aid of a Cary 81 spectrometer, equipped with a Spectra Physics No 125 helium-neon laser. The samples were filled in the $30\text{ }\mu\text{l}$ capillary cells and semiquantitative polarization measurements of iodocyclohexane were carried out. No discolouring of iodocyclohexane was observed on irradiation with the 6328 \AA laser frequency.

RESULTS AND DISCUSSION

The infrared and Raman frequencies which were observed in the fundamental region $3000-2800$ and below 1500 cm^{-1} for chloro, bromo, and iodocyclohexane are listed in Tables 1-3, respectively. Some Raman bands and a great many infrared frequencies were observed outside these regions. They can all be explained as overtones or combination frequencies, but to prevent excessively long tables these frequencies have been omitted. The present infrared and Raman frequencies of liquid chloro and bromocyclohexane agree fairly well with our earlier values.¹ However, the much better resolution of the modern grating spectrometers resulted in the appearance of doublets and shoulders which were formerly unobserved. In spite of the low volatility of the halogeno cyclohexanes, reasonably good vapour spectra were obtained

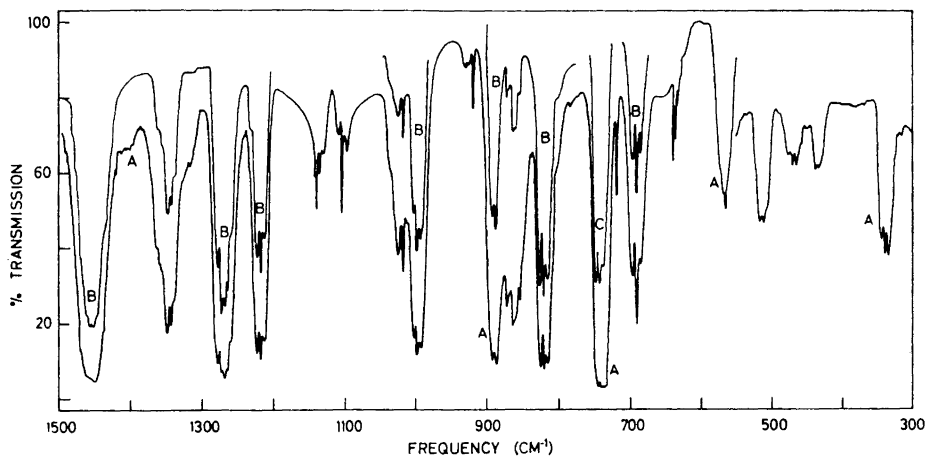


Fig. 1. The infrared spectrum of chlorocyclohexane vapour, saturation pressure, path lengths: A, 10 m; B, 4.6 m; C, 2.8 m.

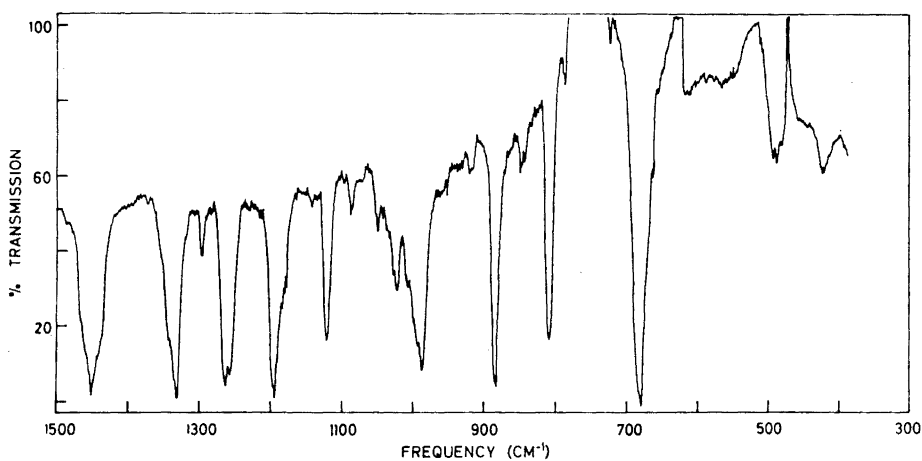


Fig. 2. The infrared spectrum of polycrystalline bromocyclohexane at ambient temperature, pressure approximately 30 kbar.

of the chloro and bromo compounds with the 10 m cell as apparent from Fig. 1. Among the 48 fundamental frequencies expected for the halogenocyclohexanes 32 should fall below 1400 cm^{-1} (the CH stretching and CH_2 scissoring modes excluded). Approximately 40 infrared or Raman bands assumed to be fundamentals were observed in the liquid state below 1400 cm^{-1} . The obvious explanation for this number of vibrational bands is the equilibrium of two conformations in the gaseous and the liquid states. Although

Table 1. Infrared and Raman spectral data ^a of chlorocyclohexane.

Vapour	Infrared		solid (30 kbar)	Raman liquid	Conformer	
	liquid	solid (-180°)				
2950 vs ^b bd	2947 vs	2943 vs		2948 vs		
	2930 vs	2925 vs				
	2905 m, sd	2905 m		2903 m		
	2895 m, sd	2895 m				
2870 s, bd	2860 vs	2856 vs		2860 vs		
	1475 m, sd					
1462 s	1452 vs	1456 s	1454 w, sd	1453 m		
1457 vs						
1452 s						
1444 vs	1448 vs	1445 vs	1447 vs	1447 s		
1441 s						
1434 w	1440 m, sd	1439 w				
1428 w	1428 w	1423 w				
1364 s	1353 s	1353 s, sp	1353 s	1350 m, sd		
1349 s	B ^c	1339 s	1338 s	1336 s	1339 s	
1343 s			1334 m			
			1320 w	1324 w		
			1302 vw	1301 m, sp	1301 w	
1279 vs	B	1267 vs	1268 vs, sp	1266 vs	1270 s	
1273 vs						
1267 vs	A/C	1259 vs	1254 vs, sp	1252 vs	1261 vs	
1263 vs						
1259 vs						
1223 vs	A	1214 vs	1216 vs	1217 vs	1216 m	
1218 vs						
1212 vs						
1150 w		1184 vw	1183 vw		1184 w	
		1146 w	1144 vw		1145 vw	
1142 m	A/C	1132 w	1132 m	1130 m	1131 m	
1135 m						
1130 m						
1109 m	C	1098 m	1088 m	1085 w	1095 vw	
1104 s						
1097 m						
		1087 vw	1070 w		1073 w	
		1051 vw	1049 s, sp	1050 s		
		1029 m	1030 m	1026 s	1028 vs	
			1024 s			
1025 s	A/C	1014 s	—	—	1013 w	<i>a</i> ^d
1018 s						
1012 s						
1003 vs	A/C	993 vs	993 vs	991 vs	993 s	<i>e</i>
998 vs						
992 vs						
		948 vw	939 vw		920 vw	
		921 w	918 vw			
893 vs	B	889 vs	890 vs	887 vs	888 w	
887 vs			888 vs			
872 s			—			
864 s	B	858 s	850 s	846 s		
860 s						

Table 1. Continued.

854 m, sp		852 m	—	—	851 s	<i>a</i>
826 vs)	A	817 vs	815 vs	814 vs	820 s	<i>e</i>
820 vs)						
815 vs)						
808 w		807 m	—	—	809 s	<i>a</i>
746 vs)	A	731 vs	725 vs	722 vs	732 vs	<i>e</i>
741 vs)						
735 vs)						
697 s)	C	684 s	—	—	684 s	<i>a</i>
691 s)						
685 s)						
656 w)	B?	641 w	639 w	—	—	—
651 w)						
572 w)	C	558 m	—	—	561 s	<i>a</i>
565 m)						
560 w)						
518 m)	A	512 m	512 s	512 s	513 s	<i>e</i>
513 m)						
507 m)						
476 w)	B?	472 m	—	—	473 m	<i>a</i>
471 m)						
465 m)						
459 w)	B	435 m	433 m	431 m	437 s	<i>e</i>
438 m)						
432 m)						
345 m)	A	340 m	340 s	—	339 vs	—
340 m)						
335 m)						
		335 w, sd	330 s			
		328 vw				
		324 vw				
		302 vw				
280 w		284 w, bd	—		286 s	<i>a</i>
		258 m	257 s		261 vs	<i>e</i>
					146 s	

^a Only bands in the fundamental regions 3000–2800 and below 1500 cm⁻¹ are included.

^b The following abbreviations have been used: s, strong; m, medium; w, weak; v, very; sp, sharp; bd, broad and sd, shoulder.

^c A, B, and C denote band contours.

^d *a*, axial halogen; *e*, equatorial halogen.

they both have the same symmetry (point group C_2) the molecules with equatorial or axial halogens each should have a separate set of vibrational fundamentals. However, the number of bands observed reveal that the majority of the infrared and Raman bands must be assigned to both conformers. Only certain bands, and particularly those connected with stretching and bending of the C—X linkage or certain skeletal modes seem to be sufficiently unlike for the *e* and the *a* conformers to appear as distinct, separated bands. The large number of methylene stretching and bending modes on the other hand apparently coincide completely for the two conformers, thus giving rise to only one observable infrared or Raman band.

Table 2. Infrared and Raman spectral data ^a of bromocyclohexane.

Vapour	Infrared liquid	solid (-170°)	solid (30 kbar)	Raman liquid	Conformer
2954 vs ^b bd	2935 vs 2905 w sd 2885 w, sd	2925 vs 2905 w, sd		2943 vs 2905 w	
2872 vs, bd	2857 s 2836 w, sd 1463 m 1449 vs	2858 s 1463 m 1453 vs 1442 vs	1450 vs	2860 s 2835 m 1447 vs	
1355 w 1344 s 1340 s 1336 s	A 1335 s	1328 s, sp	1330 s	1345 vs 1336 s	
1303 w 1298 w	B 1322 vw, sd 1298 w 1270 vw, sd 1256 s, sd	1321 vw 1303 m 1299 m 1268 vw 1257 s	1295 m 1262 s	1299 w 1256 s	
1263 vs 1257 vs 1251 vs 1198 vs 1195 vs 1190 vs	A 1252 vs 1191 vs 1142 vw	1253 s 1197 vs 1187 w 1141 vw?	1253 s 1197 vs 1141 vw	1191 s 1145 vw	
1125 s 1121 s 1117 s 1095 m 1091 m 1087 m	A/C 1117 s 1086 m 1049 vw 1028 w	1120 vs 1086 m 1070 m 1049 m, sp 1026 m	1120 vs 1085 m 1050 m 1024 w	1120 w 1087 w 1051 w 1028 s	
1019 s 1013 s 1010 s 996 s 993 s 988 s	A/C 1010 m A 988 s	— 991 s	— 990 s	1010 w, sd 989 s	<i>a</i> <i>e</i>
889 vs 884 vs	B 963 w 919 w 885 vs 864 m	961 vw 917 w 889 vs 885 vs —	917 w 889 vs 885 vs —	887 w	<i>a</i>
859 s 855 s 850 s 816 vs 812 vs 807 vs	A/C 852 s A 810 vs	845 w 811 vs	845 w 809 vs	849 s 808 vs	<i>e</i>

Table 2. Continued.

		804 m	790 w	787 w		
		771 w	—	—		
		735 w	735 w			
700 vs)						
697 vs)		687 vs	683 vs	680 vs	687 vs	<i>e</i>
693 vs)						
665 s)						
660 s)	C	658 s	—	—	660 s	<i>a</i>
655 s)						
519 m)						
515 m)	A/C	513 w,sd	—	—	514 w,sd	<i>a</i>
510 m)						
506 m)	B	500 m	498 s	496 s	503 vs	<i>e</i>
501 m)						
461 m)		458 m	—	—	460 vs	<i>a</i>
		437 w	438 w	436 w		<i>e</i>
		427 w	428 w	424 w	428 vs	
		367 vw	—	—	370 s	<i>a</i>
		327 vw	325 vw	—	327 s	<i>e</i>
		261 m	259 s	—	262 vs	
		218 w	—	—	219 s	
					187 w	
					130 s	

^a Only bands in the fundamental regions 3000–2800 cm⁻¹ and below 1500 cm⁻¹ are included.

^b For abbreviations, see footnotes to Table 1.

Low temperature spectra. As described previously¹ a number of infrared bands in chloro and bromocyclohexane disappear in the solid, crystalline state at low temperature. Primarily, based upon the C—X stretching bands, it was concluded from these data that only the *e*-conformer exists in the truly crystalline state, although chlorocyclohexane passes through a cubic modification after freezing in which both conformers are present. Because of experimental limitations the previous low temperature spectra were recorded only in the sodium chloride region, while the present investigations reached down to 240 cm⁻¹. Various new bands, disappearing in the solid state, were detected. For iodocyclohexane, such investigations have not previously been reported, and it appears from Table 3 that several bands vanished in the solid. It is well known from a variety of experimental techniques^{2,8} that an equatorial group has a higher C—X stretching frequency than an axial group. Therefore the 657 and the 642 cm⁻¹ bands can with confidence be assigned to the *e* and the *a*-conformers, respectively. Since the latter disappears in the solid, iodocyclohexane like chloro- and bromocyclohexane crystallizes as pure *e*-conformer at low temperatures.

High pressure spectra. The three halogeno cyclohexanes formed a spontaneous polycrystalline solid when compressed to approximately 40 kbar pressure. By careful releasing the pressure until only one crystallite was present and then gradually increasing the pressure, a single crystal can easily be grown in the high pressure cell. These manipulations can conveniently be carried out⁷ under a polarization microscope. A considerable “superpressing” is generally observed, and the spontaneously formed polycrystalline solid can

Table 3. Infrared and Raman spectral data ^a of iodocyclohexane.

Liquid	Infrared solid (−170°)	Infrared solid (30 kbar)	Raman liquid	Conformer
2934 vs ^b			2940 vs	P ^c
2910 w, sd			2919 w, sd	P
2885 vw			2883 w	D
2857 s			2855 s	P
2835 w			2833 m	D
1460 w	1464 s, sp		1463 m, sd	
1446 vs	1450 vs	1450 vs	1447 s	D
1436 w	1443 vs		1435 w	
1426 m	1425 s		1425 w	
1354 vw, sd	1354 m, sp			
1347 s	1349 s, sp}	1347 s	1348 w,	D
1330 s	1344 s, sp}		1333 s	P
	1331 s		1319 w	D?
1294 w	1295 m		1298 m	D
1267 w, sd	1266 w		1270 m	D
1253 vs	1255 vs	1255 vs	1256 s	P <i>e</i>
1242 vs	—	—	1247 m	P <i>a</i>
1175 vs	1178 vs	1177 vs	1175 s	P <i>e</i>
1167 vs	—	—	1167 m	P <i>a</i>
	1106 w			
1094 vs	1096 vs	1096 vs	1096 m	D
1074 w	1082 s}	1078 s	1074 w	D
	1071 s}			
1044 vw	1047 w		1051 vw	
1030 m	1023 m	1024 w	1032 s	D <i>e</i>
1021 w	—	—	1023 s	D <i>a</i>
1006 s	—	—	1008 vw	P <i>a</i>
	993 vs}	990 vs	988 s	P <i>e</i>
988 vs	988 vs}			
915 w	917 m	916 m	918 vw	
883 s	882 vs	881 vs	884 m	D
862 m	—	—	866 m	P <i>a</i>
848 m	842 m	842 m	847 s	P <i>e</i>
806 s	808 s	807 s	806 s	D
784 vw?	788 m	785 m		
712 vw	712 vw			
657 s	653 vs	652 vs	658 vs	P <i>e</i>
642 s	639 w	—	641 m	P <i>a</i>
582 w	—	—		
493 m	493 m}	490 m	493 s	P
	487 m}			
445 m	—		448 s	P <i>a</i>
438 w	435 m	437 w	436 w	P <i>e</i>
422 vw	422 w		422 m	D
357 vw	—		359 s	P <i>a</i>
321 vw	319 w		323 m	P <i>e</i>
235 vw			238 w	P <i>a</i>
219 s	216 vs		223 vvs	P <i>e</i>
			197 w	D
			109 m	

^a Only bands in the fundamental regions 3000–2800 cm^{−1} and below 1500 cm^{−1} are included.

^b For abbreviations, see footnotes to Table 1.

^c P, Polarized; D, depolarized.

Table 4. Tentative vibrational fundamentals in halogenocyclohexanes.

Cl		Br		I		Suggested motion	
Infrared ^a	Raman	Infrared ^a	Raman	Infrared ^b	Raman		
2950 vs ^c	2948 vs	2954 vs	2943 vs	2934 vs	2940 vs	} CH ₂ and CH stretch	
2930 ^b vs					2919 w		
2905 ^b m	2903 m	2905 ^b w	2905 w	2910 w	2904 w		
2895 ^b m		2885 ^b w		2885 vw	2883 w		
2870 s	2860 vs	2872 vs	2860 s	2857 s	2855 s		
		2836 ^b m	2835 m	2835 w	2833 m		
1475 ^b m		1463 ^b m		1460 w	1463 m		
1457 vs	1453 m	1455 s	1447 vs	1446 vs	1447 s		
1444 vs	1447 s						
1434 w		1436 ^b m		1436 w	1430 m		} CH ₂ scissor
1428 w				1426 m			
1364 s	1350 m	1355 w	1345 vs	1347 s	1348 w		
1346 s	1339 s	1340 s	1336 s	1330 s	1333 s		
1320 ^b w		1322 vw			1319 w		
1302 vw	1301 w	1300 w	1299 w	1294 w	1298 m		
1276 vs	1270 s	1270 ^b vw		1267 w	1270 m		
				1253 vs	1256 s		
1263 vs	1261 vs	1257 vs	1256 s	1242 vs	1247 m	} CH ₂ wag CH ₂ twist CH def	
				1175 vs	1175 s		
1218 vs	1215 m	1195 vs	1191 s	1167 vs	1167 m		
1135 m	1131 m	1121 s	1120 w	1094 vs	1096 m	} ring stretch	
1104 s	1095 vw	1097 m	1075 w?	1074 w	1074 w		
1087 ^b vw	1073 w						
1051 ^b vw	1050 s	1049 ^b vw	1051 w	1044 vw	1051 vw		
1029 ^b m	1028 vs	1028 ^b w	1028 s	1030 w	1032 s		
				1021 w	1023 s		
1018 s		1013 s		1006 s	1008 vw		
998 vs	993 s	993 s	989 s	988 vs	988 s		
921 ^b w	920 vw	919 w		915 w	918 vw		
890 vs	888 w	887 vs	887 w	883 s	884 m		} CH ₂ rock
872 s		864 ^b m		862 m	866 m		
862 s		855 s	846 s	848 m	847 s	} ring stretch	
854 m	851 s						
820 vs	820 s	812 vs	813 vs	806 s	806 s	} CH ₂ rock C-X stretch ring bend	
808 w	809 s	804 m	806 vs	775 vw			
741 vs	732 vs	697 vs	687 vs	657 s	658 vs		
691 s	684 s	660 s	660 s	642 s	641 m		
565 m	561 s	515 m		493 m	493 s		
513 m	513 s	503 m	504 vs				
468 m	473 m	461 m	461 vs	445 m	448 s		
435 m	437 s	437 ^b w		438 w	436 w		
340 m	339 vs	427 w	428 vs	422 vw	422 m		
		367 vw	371 s	357 vw	359 s		
		327 vw	327 s	321 vw	323 m		
280 w	286 s	261 m	262 vs	235 vw	238 w	} C-X bend	
258 ^b m	261 vs			219 s	223 vvs		
		218 w	219 s		197 w		
	146 s		130 s		109 m		

^a Vapour phase frequencies, except when denoted.

^b Liquid state frequencies.

^c For abbreviations, see footnotes to Table 1.

be released to approximately 20–25 kbar at ambient temperature before the melting starts.

Infrared spectra were recorded simultaneously of the polycrystalline solids and of the single crystals. In each case the pressure was standardized to approximately 30 ± 5 kbar when the spectra were recorded. For each of the halogenocyclohexanes the polycrystalline solid and the single crystals gave practically identical spectra. In the single crystals the *a* conformer bands were completely absent, while a small residue of the *a*-conformer persisted in the polycrystalline high pressure solid. It should be emphasized that in the low-temperature polycrystalline solids as well, a complete absence of one conformer is hardly ever achieved, even after prolonged annealing. The high pressure spectrum of polycrystalline bromocyclohexane is shown in Fig. 2. It appears from this figure as well as from the listed frequencies in Tables 1–3 that the high pressure solids consisted of molecules in the *e*-conformation. Unlike the results reported by Brasch⁵ on halogenated ethanes where the *trans* or *gauche* rotamer might crystallize from the same compound by varying the experimental conditions, we never succeeded in crystallizing an *a*-conformer. Various procedures were attempted: the sample was simultaneously pressurized and cooled by immersing the diamond cell in a dry ice-acetone mixture or in liquid nitrogen. Moreover, the sample was pressurized prior to or after cooling, but the crystals consisted persistently of the *e*-conformers. Evidently, the *a*-conformer of these halogenocyclohexanes is thermodynamically unstable in the crystals. The present infrared and Raman intensity data strongly suggest that the *e*-conformer is more stable than the *a*-conformer in the vapour and in the liquid, which is in agreement with earlier electron diffraction⁹ data of the vapours and PMR¹⁰ measurements in solution. In addition, variations of the molar volume with pressure $(\partial v/\partial p)_T$ seemingly favors the existence of the *e*-conformers for these three molecules. It might be added that for other halogenated cyclohexanes, *e.g.* the *trans* 1,2-dihalogenocyclohexanes,^{11,12} the dichloro compound crystallizes in (*e,e*), the dibromo compound in (*a,a*). High pressure studies of these molecules are presently being carried out.

Spectral correlations. The infrared and Raman frequencies observed in the spectra of chloro-, bromo-, and iodocyclohexane which are believed to be fundamentals, are collected in Table 4. A striking similarity between the spectra of the three compounds is evident. The vibrational modes seem to occur at approximately the same frequencies in each of the molecules, except for the vibrations mainly connected with the C–X stretching or bending modes for which mass sensitive shifts were observed. Generally, the bands that are split into separate components for the *e*- and the *a*-conformers fall in regular patterns for these molecules. There are, however, some notable exceptions to this. Thus, the infrared bands assigned to the *a*-conformer at 1242, 1167, and 1022 cm^{-1} in iodocyclohexane had no equivalents in the other molecules. These three *a*-conformer bands and what we believe to be the corresponding *e*-conformer bands were separated less than 11 cm^{-1} in iodocyclohexane, but apparently overlapped in the spectra of the other molecules. On the other hand, the infrared and Raman bands at 493 cm^{-1} in iodocyclohexane seem to be common for both conformers, while the bands at 565 and 515 cm^{-1} in the chloro- and bromocyclohexane, respectively, belonged to the

a-conformer and those of the *e*-conformer had a lower frequency. Finally the infrared and Raman bands at 261 and 262 cm^{-1} , respectively, in bromocyclohexane were common to both conformations, although it appears from Table 4 that the chloro- as well as the iodocyclohexane had bands which were split into the two conformers in this region. It seems as if an axial or equatorial substituent had a somewhat larger effect on the vibrational spectra for the heavy iodine judged from the number of split bands. On the other hand, the frequency difference between the *e*- and the *a*-conformer bands were smallest for iodo compound and largest for chloro compound.

Because of the large number of fundamentals and the low symmetry (C_s) of the molecules no assignment of the bands into A' or A'' species have been attempted, although the infrared vapour phase band contours and the Raman polarization data would be of considerable help. From the low temperature and the high pressure infrared spectra, the pure *a*-bands can be sorted out, but considerable uncertainty exists as to which bands represent pure *e* and which bands are a overlapping *e* and *a*. However, the vapour phase contours, particularly for chlorocyclohexane gave some clue to this problem. Thus, the corresponding pairs of *e* and *a* bands appear with identical contours and approximately the same shoulder separation. An approximate calculation of the principal moments of inertia for the two conformers in connection with the Badger and Zumwalt calculations¹³ support these experimental results. Moreover, since the *e* and the *a* conformers have identical symmetry, the equivalent vibrational modes for the two conformers must belong to identical species A' or A'' . Accordingly, they should both be polarized or both depolarized in Raman, although for the polarized bands the polarization ratio might be somewhat different between them.

Some of the weaker bands from Tables 1–3 have not been included in Table 4, although they might be fundamentals. A tentative classification of the vibrational modes into methylene stretching, scissoring, wagging, twisting, and rocking as well as skeletal stretching and bending has been attempted in Table 4. This description corresponds reasonably well with the assignments for cyclohexane itself,¹⁴ but the modes in the halogenocyclohexanes are undoubtedly highly mixed.

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