Vibrational Spectroscopic Studies of Some

trans-1,2-Dihalocyclohexanes

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The IR spectra of *trans*-1,2-dichloro-, bromochloro-, and dibromo-cyclohexane were recorded in the region $4000-200$ cm^{-1} as liquids, in polar and unpolar solvents, in the crystalline state at low temperatures, and partly at room temperature under high pressure. Raman spectra of the three molecules were obtained as pure liquids and when dissolved in polar and unpolar solvents.

trans-1,2-Dichloro-, bromochloro-, and dibromocyclohexane crystallized at low temperatures in the *ee*, *ee*, and *aa* conformations, respectively, and under high pressures in *ee*, *aa*, and *aa*. A quite reliable attribution of the stronger vibrational bands into the *ee*, *aa* or *ee* and *aa* conformations was carried out. The large majority of the vibrational bands below 1400 cm^{-1} belonged to one of the conformers only. A remarkable similarity between the spectra of the three molecules was observed. Some skeletal modes around 1000 cm^{-1} clearly suitable for diagnostic purposes have been compared with the data for other halogenated cyclohexanes.

Since the pioneering work of Hassel [1] the structure of cyclohexane derivatives are now quite well understood. A large bulk of information regarding the conformational equilibrium of these molecules in the vapour, liquid and dissolved states have accumulated, and this material is reviewed in two monographs.[2,3] A variety of physical methods have been employed such as diffraction methods, microwave, vibrational, and NMR spectroscopy, dipole and ultrasonic methods in addition to equilibration and reaction rate studies. Generally, molecules containing equatorial are more stable than those having axial substituents [2,3] because of the 1,3-diaxial repulsion. However, for di- or polyhalogenated cyclohexanes, the dipole-dipole repulsion between vicinal *e* substituents might instead stabilize the conformations containing axial substituents.

We have been interested in the halocyclohexanes for a long time, and following the work by Kohlrausch and Stockmair,[4] Larnaudie [5] and Kozima [6] we reported vibrational spectroscopic studies of some mono- [7] and 1,2-dihalocyclohexanes [8] more than a decade ago. In agreement with the results from dipole moment studies [6,9–12] the spectroscopic work [6,8] revealed that the

conformational equilibrium for the *trans*-1,2-dihalocyclohexanes are highly influenced by the solvent polarity. Moreover, while the dichloro compound crystallizes in the *ee*, the dibromo derivative exists in the *aa* conformation in the crystalline state at low temperatures.

We felt it would be of interest to extend these studies to include the *trans*-1,2-bromochlorocyclohexane (BCC). Furthermore, with the aid of a high pressure cell with diamond windows,[13] the high pressure crystalline solids can be investigated. The low temperature and the high pressure solids can consist of different conformations, as reported for some halogenated ethanes.[14] With the modern infrared grating and the Raman laser spectrometers, much better spectra can be obtained than what was previously possible, and a quite thorough study of the vibrational spectra of these molecules is now possible.

In the present communication we shall report the spectral data for BCC as well as for the *trans*-1,2-dichloro (DCC) and *trans*-1,2-dibromocyclohexane (DBC). New spectral data for the monohalocyclohexanes have recently been published,[15] and the results for *trans*-1,4-dihalocyclohexanes as well as for *trans*-1,2-chloroiodocyclohexane [16] will be published shortly.

EXPERIMENTAL

The samples of DCC and DBC were prepared by the same procedure as described earlier [8] and the purities were checked by gas chromatographic analysis. BCC was synthesized by adding hypobromous acid to cyclohexene, and the formed bromocyclohexanol was subsequently treated with phosphorus pentachloride to give the compound.[17] The sample was repeatedly fractionated under reduced pressure (b.p. 94°/17 torr) and finally purified by preparative gas chromatography. The solvents, carbon tetrachloride, carbon disulphide, and acetonitrile were of spectroscopic grade (Uvasole, Merck) and were not purified further.

The infrared spectra were recorded in the region 4000 − 200 cm^{-1} with a Perkin-Elmer model 225 spectrometer. The samples were studied as pure liquids and in solution at room temperature, while the low temperature spectra were obtained using a cell from RIIC, cooled with dry ice and equipped with Cs I windows. For the high pressure experiments, a cell [13] with type II diamonds was used in connection with a Perkin-Elmer 4X beam condenser. The samples were contained in a hole of approximately 0.3 mm diameter drilled in a spacer of stainless steel. Because of the small sample size, fairly wide slits, high gain and low recording speed was necessary for these measurements. Attempts were made to record the vapour spectra, but only the strongest bands in DCC were detected with a 10 m gas cell at room temperature.

Raman spectra were recorded with the aid of a Cary 81 spectrometer, equipped with a Spectra Physics No. 125 helium-neon laser. The 180° illumination technique was employed, and the pure liquids and the solutions were filled into capillary cells of 0.5 mm ID. We have reported [8] the polarization ratios for the stronger Raman bands in DCC and DBC, but these values can be determined much more accurately with laser excitation. A 2.5 ml multiple reflection cell was employed with 90° illumination for these measurements.

RESULTS AND DISCUSSION

The infrared absorption spectra of DCC as a liquid and as crystalline solids at low-temperature and high pressure are shown in Figs. 1, 2, and 3, respectively. Correspondingly, IR spectra of BCC and DBC as liquids are given in Figs. 5 and 8, the low temperature spectrum of BCC appears in Fig. 6, and the high pressure spectrum of DBC in Fig. 9. Raman spectra of the liquids are shown in Figs. 4, 7, and 10 for DCC, BCC, and DBC, respectively, The infrared and Raman frequencies observed below 3000 cm^{-1} are listed in Tables 1 − 3 for the three molecules. These data agree quite well with our earlier list of frequencies [8] for DCC and DBC, but several new doublets and shoulders were observed, and the IR frequency region was considerably extended. The Raman spectra did also reveal various details not previously observed by photographic technique, and the solvent studies were successfully applied to the Raman spectra. For BCC, only a few vibrational frequencies have previously been reported.[18]
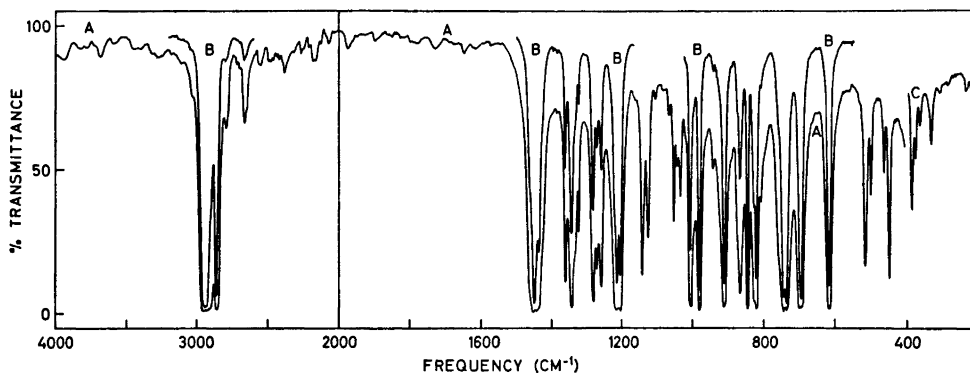

Fig. 1. IR spectrum of liquid *trans*-1,2-dichlorocyclohexane. A, 0.1 mm KBr cell; B, 0.025 mm KBr cell; and C, 0.2 mm polyethylene cell.

Fig. 2. IR spectrum of polycrystalline *trans*-1,2-dichlorocyclohexane (− 140°).

Fig. 3. IR spectrum of a single crystal of *trans*-1,2-dichlorocyclohexane at ambient temperature (*ca.* 30 kbar pressure).

Fig. 4. Raman spectrum of liquid *trans*-1,2-dichlorocyclohexane.

Fig. 5. IR spectrum of liquid *trans*-1,2-bromochlorocyclohexane. A 0.1 mm KBr cell; B, 0.025 mm KBr cell; and C, 0.2 mm polyethylene cell.
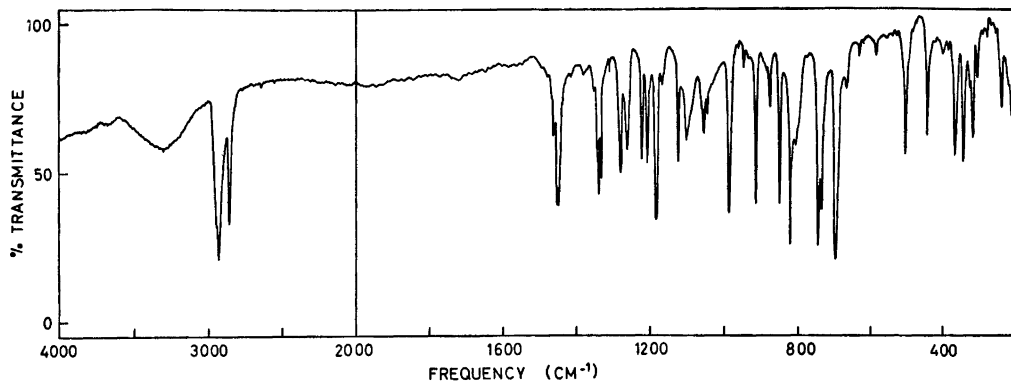
Fig. 6. IR spectrum of polycrystalline *trans*-1,2-bromochlorocyclohexane (− 140°).
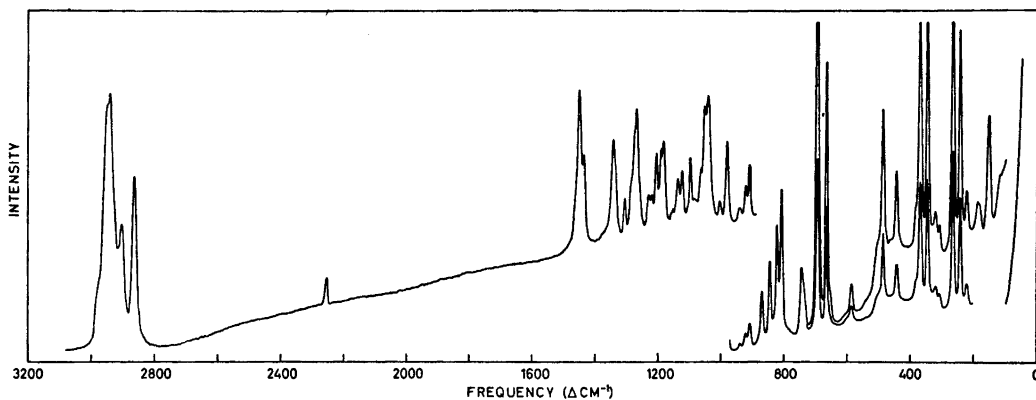
Fig. 7. Raman spectrum of liquid *trans*-1,2-bromochlorocyclohexane.
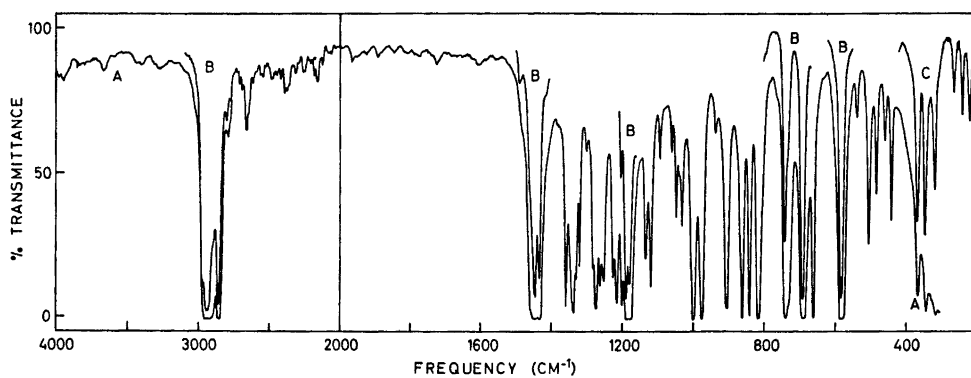
Fig. 8. IR spectrum of liquid *trans*-1,2-dibromocyclohexane. A, 0.1 mm KBr cell; B 0.025 mm KBr cell; and C, 0.2 mm polyethylene cell.
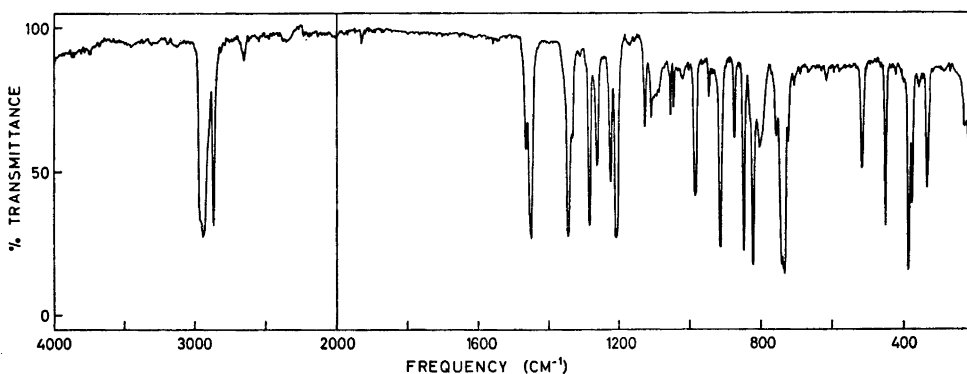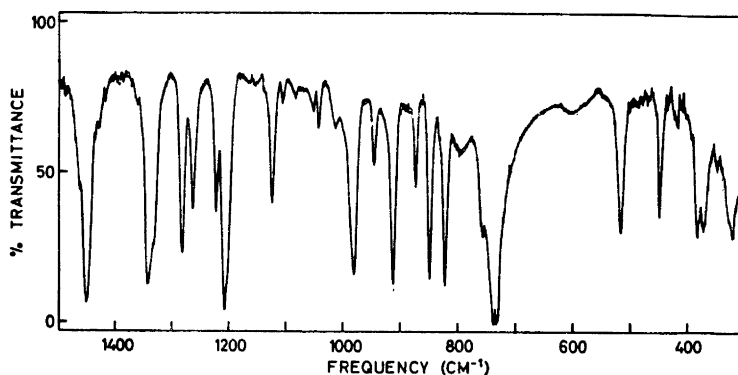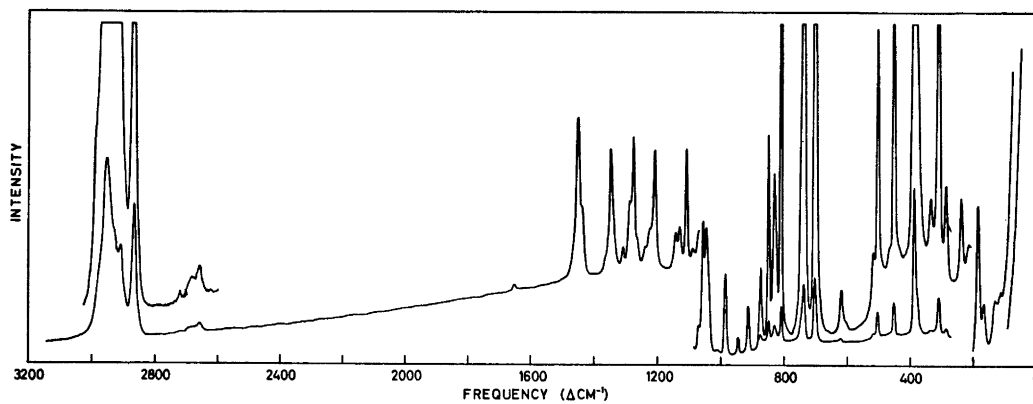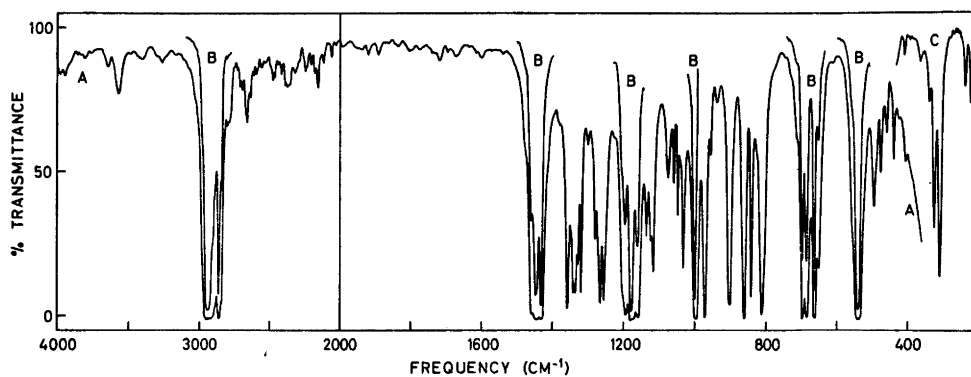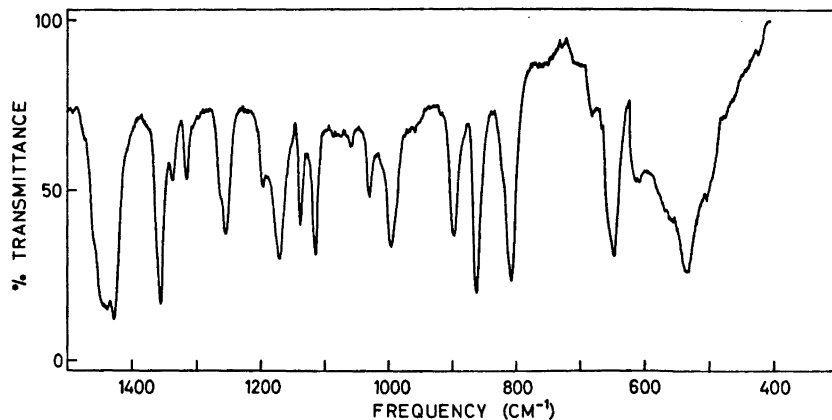
Fig. 9. IR spectrum of a single crystal of *trans*-1,2-dibromocyclohexane at ambient temperature (*ca.* 30 kbar pressure).
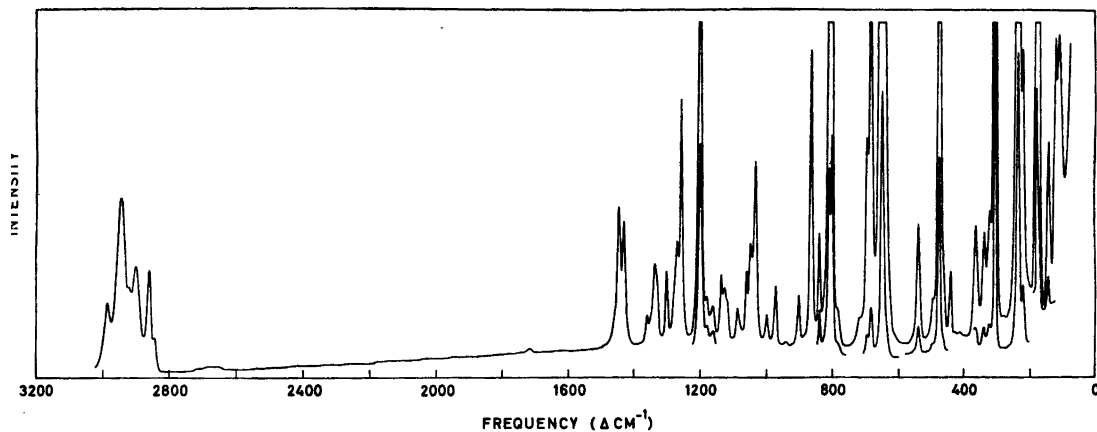
Fig. 10. Raman spectrum of liquid *trans*-1,2-dibromocyclohexane.

With 18 atoms, the present molecules should have 48 fundamental frequencies for each conformer. However, with 10 hydrogens, we expect several of the CH_2 stretching and scissoring vibrations to overlap, since these modes are crowded together around 2900 and 1450 cm^{-1}, respectively. It is even less likely that these vibrations should be sufficiently separated for the *ee* and the *aa* conformers to appear as separated bands. Thus, we might expect approximately $34 - 32$ vibrational bands for each conformer below 1400 cm^{-1}. Since *ca.* 54 infrared or Raman bands, considered to be fundamentals, were observed in this region, a rough estimate gives 20 vibrational modes for each conformer appearing as distinct bands, whereas 14 bands may be assigned to overlapping

fundamentals for both conformers. As a comparison, only *ca.* 40 bands were observed below 1400 cm^{-1} for the monohalocyclohexanes.[15] Therefore, many more vibrational bands of the two conformers coincide for the mono than for the *trans*-1,2-dihalocyclohexanes. This is not surprising, since the latter group of molecules have *two* substituents in non-equivalent positions compared to *one* in the monohalocyclohexanes. It should be noted that a comparatively larger number of vibrational bands are common to both the *trans* and the *gauche* conformers in non-cyclic halogenated hydrocarbons like, *e.g.* the chlorinated[19] or brominated[20] propanes.

(a) *Solution spectra.* As observed from dipole,[6,9-12] Raman[6] and infrared,[8] studies, the conformational equilibrium in the *trans*-1,2-dihalocyclohexanes is highly dependent upon the solvent polarity. As extensively studied by Bernstein *et al.*[21] for halogenated ethanes, the more polar conformer is favoured in solvents of high dielectric constants. For the present molecules, the *ee* conformers are expected to have dipole moments close to the *cis*-1,2-dihalocyclohexanes around 3.1 D.[9] A surprisingly large dipole moment around 1.2 D has been measured[22] for the *trans*-1,2-dihalocyclohexanes, in which the *aa* conformers have been fixed with an equatorial *t*-butyl group in the 4-position. These values have been interpreted in terms of an angle between the C-Hal bonds, considerably lower than 180°, but fairly constant for the three present molecules.[22]

In agreement with the large dipole difference between the *ee* and the *aa* conformers, a large displacement of the conformational equilibrium with solvent polarity was detected from infrared data using 10 different solvents.[8] Our present aim was to classify the vibrational bands into *ee*, *aa*, or *ee*+*aa*. The non-polar and the highly polar solvents CCl_4 and CH_3CN, respectively, were employed for the infrared as well as for the Raman recordings, and the relative band intensities were compared with those of the pure compounds. Thus, the bands increasing or decreasing in intensity in the order CCl_4 − pure liquid − CH_3CN were denoted as *i* or *d*, respectively, in Tables 1 − 3. For some lines, no intensity variations were observed, probably because they had contributions from both conformers. In other cases, the bands were too weak or they fell in regions of strong solvent bands, and no attributions could be made. In practically all instances, the *i* and *d* bands extracted from the infrared spectra agreed with those from the Raman and *vice versa*. Exceptions are the infrared bands at 1041 and 873 cm^{-1} in DCC, and at 1448 and 1300 cm^{-1} in DBC and their Raman counterparts. Obvious explanations to the latter effects are offered by bands common to both conformers in which, *e.g.*, the *ee* and the *aa* conformers have the higher extinction coefficients in the infrared and Raman, respectively.

(b) *Low temperature spectra.* The enthalpy difference between the *ee* and the *aa* conformers for the present molecules can be estimated from the dielectric measurements in the vapour[23] and in solution[9-12] and from NMR data.[24] A variation in the infrared and Raman band intensities with temperature has been reported for DBC,[25] but because of the small effect, these variations have limited diagnostic value.

A drastic simplification in the spectra of DCC and DBC at low temperatures have been observed,[6,8] since only one conformer is present in the crystalline

Table 1. Infrared and Raman spectral data of *trans*-1,2-dichlorocyclohexane.

Infrared [a]			Raman		Con-former	Species
Liquid [b]	Solv.[c] eff.	Solid [d] −70°	Liquid [b]	Solv.[c] eff.		
3035 vw						
			2975 w,sd D			B
2960 m,sh		2961 vs				
2945 vw,bd		2939 vs	2951 vs,bd P			A
			2925 s D			
2905 m,sh		2903 m,sd	2906 s P			A
			2890 w,sd D			B
2863 s		2866 s	2863 vs P			A
			2850 w,sd			
2796 w						
2666 w		2654 w				
1646 vw			1645 vw			
1460 vw,sh		1463 m			ee aa	
1449 vs	i	1448 vs	1446 s D	i	ee	B
1436 s	d	*	1433 m D	d	aa	B
1360 s	d	*	1360 vw	d	aa	
1343 vs	i	1343 vs	1342 s P	i?	ee	A
1331 w,sh		1330 w	1332 w,sd D?		ee	B?
1322 w	d	*			aa	
1304 vw			1303 vw	d	aa	
1280 s	i	1281 s	1283 m D?	i	ee	B
1271 m	d	*	1271 s P	d	aa	A
1257 m	i	1260 m	1260 vw D	i?	ee aa	B
			1233 vw	d	aa	
1220 m,sh		1221 s	1221 vw P	i	ee	A
1214 vs	d	*	1213 vw		aa	
1204 vs	i	1204 vs	1203 s P?	i	ee	B
1140 s	d	*	1136 m P	d	aa	A
1135 w,sh	d				aa	
1124 m	i	1123 m	1125 m D	i	ee	B
1102 vw		1106 m	1103 s P	i	ee	A
			1084 vw D			B
1064 vw	d	*	1065 vw D		aa	B
1050 m	i	1050 m	1051 s P?	i	ee	A
1041 m	i	1043 m	1040 s D		ee	B
1032 m	d	*	1033 m D		aa	B
1005 vs	d	*	1006 vw D		aa	B
980 vs	i	983 vs	981 s D	i	ee	B
941 w		945 w	942 m D	d?	ee aa	B
909 vs	i	912 vs	910 m P		ee	A
888 vw		*			aa	
873 vw	i	872	871 m P?	d	ee aa	A?
865 s	d	*	863 vw		aa	
845 vs	i	845 vs	845 s P	i	ee	A
826 s	d	*	827 s P	d	aa	A
820 vs	i	821 vs	821 w	i	ee	
806 vw	d	802 w	806 s P	d	ee aa	A
758 w,sh	d?	756 m			ee aa	
743 vs	i	739 vs	744 w,sd D		ee	B
736 vs	i	733 vs	735 vs P	i	ee	A

Table 1. Continued.

698 m,sh	d	*			aa	A
695 vs	d	*	700 vs P	d	aa	A
662 vw		663 vw			ee	
616 vs	d	*	616 w D?		aa	B?
514 s	i	514 s	514 w D		ee	B
498 m	d	*	498 s P		aa	A
462 m	d	*	461 vw D		aa	B
447 s	i	448 s	447 vs P		ee	A
384 vs	i	384 vs	384 vs P	i	ee	A
374 s	i?	374 s	375 m,sh D?		ee aa	B?
361 s	d	*	361 w,sh		aa	
331 s	i	330 s	331 w D	i	ee	B
307 vw		*	307 vs P	d	aa	A
			283 m P	i	ee	A
231 m		226 w	233 m D	i	ee	B
209 s			210 w	d	aa	B
			182 vs P	i	ee	A
			164 m P		aa	A
			128 vw, bd	d	aa	
			112 vw,bd	i	ee	

[a] Very weak IR bands in the combination regions 4000—3000 and 2700—1700 cm⁻¹ are omitted.

[b] Abbreviations: s = strong, m = medium, w = weak, v = very, sh = shoulder, bd = broad, P = polarized, and D = depolarized.

[c] i and d denote increased and decreased intensities in polar solvents, respectively.

[d] Bands with an asterisk vanish in the crystalline solids.

state. It appears from Fig. 6, compared to Fig, 5. and from Tables 1 — 3 that for DCC and BCC the *d*-bands disappeared in the crystalline state, and therefore only the *ee* conformer persisted in the solid, whereas DBC exists in the *aa* conformer in the solid. Recent results [16] reveal that *trans*-1,2-chloroiodocyclohexane crystallizes in the *aa* conformer at low temperatures. The spectra of the crystalline state can therefore be employed unambiguously to assign the vanishing bands to one conformer, while the remaining bands are attributed to the other conformer, or they are common to both conformers.

(c) *High pressure spectra.* The compounds DCC and DBC spontaneously formed a polycrystalline solid when compressed to *ca.* 20 — 30 kbar pressure. When the pressure is slowly reduced, the compound gradually melts, and by increasing the pressure one remaining crystallite can be grown to form a single crystal covering the whole opening of the cell. These manipulations were performed under a polarization microscope as described by Brasch and Jakobsen.[26] The liquid is generally highly "superpressed" before the spontaneous crystallization starts and the polycrystalline solid can be released, *e.g.* to 10 — 20 kbar pressure at ambient temperature before the melting starts.

The infrared spectra of the single crystals of DCC and DBC are shown in Figs. 3 and 9, respectively. It was observed that these spectra were practically identical with those obtained from the polycrystalline solids. The high pressure spectra were recorded with large slits and a resolution of approximately 6 cm⁻¹, compared with less than 1 cm⁻¹ for the low temperature spectra. Consid-

Table 2. Infrared and Raman spectral data of *trans*-1,2-bromochlorocyclohexane.

Infrared[a]			Raman		Conformer
Liquid[b]	Solv.[c] eff.	Solid[d] −70°	Liquid	Solv.[c] eff.	
3030 w			2982 vw		
2955 w		2950 w,sh			
2940 vs		2940 s	2947 vs		
			2925 vw		
			2904 m		
2863 vs		2860 s	2862 s		
2845 w			2846 w		
2790 w					
2715 vw			2715 vw		
2694 vw			2680 vw		
2664 m					
2650 vw					
2480 vw			2651 vw		
1750 w			2480 vw		
1482 vw		1480 vw			
1455 w	d	1460 m	1461 w		ee aa
1447 vs	i	1448 s	1446 vs	i	ee
1435 vs	d	*	1431 s	d	aa
1360 s	d	*	1359 vw	d	aa
1345 m,sh					
1338 s	i?	1340 s	1339 s		ee
1330 m	i?	1328 m	1333 w	i	ee
1321 s		*	1320 vw		aa
1302 vw		1301 vw	1301 m		ee
1282 m	d	*	1281 m		aa
1275 s	i	1275 s	1271 w	i	ee
1271 w,sh	d				aa
1264 s	d	*	1263 vs	d	aa
1253 s	i	1256 s			ee
1227 m	d	*	1226 m	d	aa
1217 s	i	1218 s	1217 s	i	ee
1202 s	i	1203 s	1203 s	i	ee
1188 vs	d	*	1187 s	d	aa
1178 s	i	1178 vs	1178 vs	i	ee
1135 s	d	*	1135 m	d	aa
1120 s	i	1119 m	1120 m	i	ee
1094 w		1096 m	1094 s	i	ee
			1083 vw		
1062 w	d	*	1061 m	d	aa
1048 m	i?	1045 w	1049 s	i	ee
1032 s	d?	*	1035 s	d	aa
1000 s	d	*	1001 m	d	aa
976 s	i	985 s	976 s	i	ee
956 vw					
937 w		940 w	938 w		ee aa
906 vs	i	907 vs	906 s	i	ee
872 w		868 w			ee aa
862 vs	d	*	866 vs	d	aa
842 vs	i	844 vs	843 vs	i	ee
819 vs	d	*	819 s	d?	aa

Table 2. Continued.

815 vs	i	815 vs			ee
806 vw		802 w	805 vs	i?	ee
742 vs	i	739 vs	743 vs	i	ee
733 w,sh		729 m	734 w,sh		
692 vs	i	690 vs	692 vs	i	ee
663 s	d	*	663 vs	d	aa
651, vw,sh			652 m,sh		ee aa
630 w		625 w	624 vw		ee aa
584 vs	d	*	584 s	d	aa
539 m		*	541 vw,bd		aa
505 s	i	508 s	508 w	i	ee
484 m	d	*	485 vs	d	aa
460 m	d	*	461 w		aa
442 s	i	443 s	443 s	i	ee
406 vw,bd		400 vw			ee
368 m		365 m	368 vs		ee
344 m		343 m	345 vs	d	ee aa
		330 w			
317 m		316 m	318 s		ee
306 w		305 m	306 m		ee
262 m		*	263 vs	d	aa
240 m		238 m?	240 vs	i	ee
219 m		*	220 s	d	aa
			186 s	d	aa
			177 s	i	ee
			150 s	i	ee
			117 m		aa

[a] Very weak IR bands in the combination regions 4000−3000 and 2700−1700 cm^{-1} are omitted.

[b] For abbreviations, see footnotes to Table 1.

[c] i and d denote increased and decreased intensities in polar solvents, respectively.

[d] Bands with an asterisk vanish in the crystalline solids.

ering these differences and the sharpening of the bands at low temperatures, the high pressure and the low temperature spectra are very similar. For DCC and DBC the same conformer persisted at high pressure and in the low temperature solids whereas high pressure spectra were not recorded for BCC.*

For the halogenated ethanes it is reported [14] that the *trans* or *gauche* conformers may crystallize for the same compound by varying the experimental conditions. Various procedures were attempted for the dihalocyclohexanes, the samples were simultaneously pressurized and cooled by immersing the diamond cell in dry ice or in liquid nitrogen, and they were pressurized before or after cooling. However, the crystals always consisted of the same conformers: *ee*, *aa*, and *aa* for DCC, BCC,* and DBC, respectively, regardless of the external conditions. This result corresponds with our observations for the monohalocyclohexanes [15] which persistently crystallized in the *e* conformation at low temperatures and under high pressure.

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* *Note added in proof:* An IR spectrum of crystalline BCC under high pressure has now been obtained (Horntvedt, H. T. and Klæboe, P. *Acta Chem Scand.* **25** (1971) 772) revealing the *aa* conformation in the crystal.

Table 3. Infrared and Raman spectral data of trans-1,2-dibromocyclohexane.

| Infrared [a] | | | Raman | | | Con-former | Species |
Liquid [b]	Solv. [c] eff.	Solid [d] −70°	Liquid [b]		Solv. [c] eff.		
3570 w							
2990 vw		2986 w	2986 s	P			A
2940 vs		2945 vs	2945 vs				
		2920 s	2920 vw				
2905 m, sh		2902 s	2901 vs	P			A
2860 s		2858 s	2859 s	P			A
2840 w			2843 m	P			A
		2670 vw	2678 vw				
2660 w		2660 vw	2648 vw				
2480 w			2478 vw				
2380 w,bd							
2250 w							
2155 w			2160 vw				
2115 vw			2115 vw				
			1715 m				
			1634 vw				
			1608 vw, bd				
			1578 vw				
1460 w,sh		1455 m	1458 w,sh				
1448 vs	d	1445 vs	1444 vs	D	i	ee aa	B
1433 vs	d	1433 vs	1432 vs	D	d	aa	B
1358 vs		1358 vs	1359 s	P	d?	aa	A
			1348 w				
1343 s	i	*	1346 w			ee	
1336 s	d	1338 s	1336 s	P	d	aa	A
1328 s	i	*	1330 s	D?	i?	ee	B?
1320 s	i	1317 s				aa	
1300 w	d	1305 w	1301 s	D	i	ee aa	B
1280 m	i?	*	1280 vw,sh		i	ee	
1265 s	d	1263 s	1269 m	P	d	aa	B
1255 s	i	1256 s	1255 s	P		aa	A
1225 vw	d		1226 vw			aa	
1204 vw		*				ee	
1195 s		1200 s	1197 vs	P		aa	A
1178 vs	d	1172 vs	1178 m	D	d	aa	B?
1160 m	i	*	1159 m	D	i	ee	B?
1135 m		1136 m	1136 m	P	d	aa	B
1124 m	d	1116 s	1124 m	D	d	aa	B
1116 s	i	*	1116 w		i	ee	
1090 nw		1094 w	1086 s	P		ee aa	A
1075 m		*	1074 vw,sh			ee	
1058 m		1057 m	1058 m	D?	d	aa	B?
1047 m		*	1047 s	P	i		
1032 s		1030 s	1032 s	D	d	aa	B
999 vs	d	998 vs	999 w	D	d	aa	B
972 s	i	*	971 m	D	i	ee	B
955 w		956 vw	954 vw			ee aa	B
940 vw		*	938 vw,bd			ee	
932 vw							
903 vs		900 vs	902 m	P	i	ee aa	A?

Table 3. Continued.

861 vs	d	864 vs	866 vs P	d	aa	A
840 vs	i	*	840 s P	i	ee	A
812 vs	d	810 s	812 vs P	d	aa	A
808 s,sh		*			ee	
803 m,sh	d	803 m	802 vs P	e	aa	A
710 vw		711 m	713 vw,sh		ee aa	A?
697 vs		*	696 m D	i	ee	B
685 vs		*	685 m P	i	ee	A
664 vs	d	661 vs			aa	
652 s		651 vs	651 vs P	d	aa	A
554 m,sh		555 m			aa	
540 vs		533 vs	540 s D	d	aa	B
494 m	i	*	493 vw D	i	ee	B
484 w		485 w			ee	
		481 vw				
475 m		476 m	475 vs P	d	aa	A
459 m		457 m	461 vw D		aa	B
439 m		*	439 s P	i	ee	A
			425 vw			
405 vw		*	408 vw			
			364 s P	i?	ee	A
337 vw,bd		*	337 m D	i	ee	B
321 m		321 s	321 m D	d	aa	B
306 m		*	306 vs P		ee	A
302 w,sh		302 w			aa	
			275 vw P?			A?
234 w		234 m	236 s P	d	aa	A
218 w		*	220 m D	i	ee	B
			175 vs P	i?	ee	A
			141 m P	d?	aa	B
			120 s P	i	ee	A
			108 s D	d	aa	B

[a] Very weak IR bands in the combination regions 4000—3000 and 2700—1700 cm⁻¹ are omitted.

[b] For abbreviations, see footnotes to Table 1.

[c] i and d denote increased and decreased intensities in polar solvents, respectively.

[d] Bands with an asterisk vanish in the crystalline solids.

The enthalpy difference between the *ee* and the *aa* conformers in DCC and DBC have been estimated from electron diffraction [27] and dielectric studies [23] in the vapour, and by dipole,[9–12] NMR,[24] and infrared methods,[8,25] in the liquid state. These measurements reveal that the *ee* and the *aa* conformers are slightly more stable in liquid DCC and DBC, respectively, and it is not very surprising that they crystallize in these conformers. For BCC, a very small intensity variation of the infrared bands at 1000 and 976 cm⁻¹ was detected in the temperature range from −20° to +100°, indicating a slightly more stable *aa* conformer.

(d) *Spectral correlations.* The infrared and Raman frequencies which are definitely assigned as fundamentals are listed in Table 4. For nearly all the bands we have good criteria revealing if they belong to the *ee*, *aa*, or are common to both the conformers. The spectra of the three molecules show a striking similarity. Thus, the vibrational modes seem to occur at approximately the

Table 4. Tentative vibrational fundamentals for the *trans*-1,2-dihalocyclohexanes.

trans-1,2-Dichloro-cyclohexane		trans-1,2-Bromo-chlorocyclohexane		trans-1,2-Di-bromocyclohexane		Confor-mation
Infrared [a]	Raman	Infrared [a]	Raman	Infrared [a]	Raman	
	2975 w		2982 w	2990 vw	2986 s	ee aa
ca. 2945 vs	2951 vs	2940 vs	2947 vs	2940 vs	2945 vs	ee aa
	2925 s		2925 vw	2920[b] s	2920 v	ee aa
2905 m,sd	2906 s		2904 m	2905 m	2901 vs	ee aa
2863 s	2683 vs	2863 vs	2862 s	2860 s	2859 s	ee aa
	2850 w	2845 w	2846 w	2840 w	2843 m	ee aa
1460 vw		1455 w	1461 w	1460 w	1458 w	ee aa
1449 vs	1446 s	1447 vs	1446 vs	1448 vs	1444 vs	ee aa
1436 s	1433 m	1435 vs	1431 vs	1433 vs	1432 s	aa
1360 s	1360 vw	1360 w	1359 vw	1358 vs	1359 s	aa
1343 vs	1342 s	1338 s	1339 s	1343 s	1348 w	ee
1331 w	1332 w	1330 m	1333 w	1328[c] s	1330[c] s	ee
1322 w		1321 s	1320 vw	1336 s	1336 s	aa
1304 vw	1303 vw	1302 vw	1301 m	1330 w	1301 s	ee aa
		1282 m	1281 m			aa
1280 s	1283 m	1275 s	1271 w	1280 m	1280 vw	ee
1271 m	1271 s	1264 s	1263 vs	1265 s	1269 m	aa
1257 m	1260 vw	1253 s		1255 s	1255 s	ee aa
	1233 vw	1227 m	1226 m	1225 vw	1226 vw	aa
1220 m	1221 vw	1217 s	1217 s	1204 vw		ee
1204[c] vs	1203[c] s	1202 s	1203 s	1195 s	1197 vs	ee
1214 vs	1213 vw	1188 vs	1187 s	1178 vs	1178 m	aa
1124[c] m	1125[c] m	1178 s	1178 vs	1160 m	1159 m	ee
1140 s	1136 m	1135 s	1135 m	1135 m	1136 m	aa
1124 m	1125 m	1120 s	1120 m	1116[c] s	1116[c] w	ee
		1094 w	1094 s	1124 m	1124 m	aa
1102 vw	1103 s		1083 vw	1090 vw	1086 s	ee aa
1064 vw	1065 vw	1062 w	1061 m	1058 m	1058 m	aa
1050 m	1051 s	1048 m	1049 s	1047 m	1047 s	ee
1041 m	1040 s					ee
1032 m	1033 m	1032 s	1035 s	1032 s	1032 s	aa
1005 m	1006 vw	1000 s	1001 m	999 vs	999 w	aa
980 vs	981 s	976 s	976 s	972 s	971 m	ee
941 w	942 m	937 w	938 w	932[c] vw		ee aa
909 vs	910 m	906 vs	906 s	940 vw	938 vw	ee
873 vw	871 m	872 w		903 vs	902 m	ee aa
865 s	863 vw	862 vs	866 vs	861 vs	866 vs	aa
845 vs	845 s	842 vs	843 vs	840 vs	840 s	ee
826 s	827 s	819 vs	819 s	812 vs	812 vs	aa
820 vs	821 w	815 vs		808 s		ee
806 vw	806 s	806 vw	805 vs	803 m	802 vs	ee aa
743 vs	744 w	742 vs	743 vs	697 vs	696 m	ee
736 vs	735 vs	692 vs	692 vs	685 vs	685 m	ee
698 m				664 vs		aa
695 vs	700 vs	663 s	663 vs	652 s	651 vs	aa
616 vs	616 w	584 vs	584 s	540 vs	540 s	aa
514 s	514 w	505 s	508 w	494 m	493 vw	ee
498 m	498 s	484 m	485 vs	475 w	475 vs	aa
462 m	461 vw	460 m	461 w	459 m	461 vw	aa
447 s	447 vs	442 s	443 s	439 m	439 s	ee
374 s	375 m	406 vw		405 vw	408 vw	ee

Table 4. Continued.

384 vs	384 vs	368 m	368 vs		364 s	*ee*
361 s	361 w	344 m	345 vs	321[c] m	321[c] m	*aa*
331 s	331 w	317 m	318 s	337 vw	337 m	*ee*
	283[c] m	306 w	306 m	306 m	306 vs	*ee*
307 vw	307 vs	262 m	263 vs		275 vw	*aa*
231 m	233 m	240 m	240 vs	218[c] w	220[c] m	*ee*
209 s	210 w	219 m	220 s	234 w	236 s	*aa*
	182 vs		177[c] s		175 vs	*ee*
	164 m		186 s		141 m	*aa*
	112[c] vw		150 s		120 s	*ee*
	128 vw		117 m		108 s	*aa*

[a] IR liquid frequencies, except when noted.
[b] IR frequency from low temperature solid.
[c] Frequencies outside the monotonic order.

same frequencies in each of the molecules. An expected general shift towards lower frequencies with heavier halogen substituents was observed. Corresponding bands in DCC, BCC, and DBC attributed to the same conformation were written on the same horizontal line in Table 4. Certain reversals in the frequency listings were necessary to adopt this scheme. Many of the vibrational bands listed together, undoubtedly correspond to equivalent vibrational modes in the three molecules, although this correlation should not be stressed too far. Obviously DCC and BCC have C_2 symmetry and the vibrational modes divide between the species A and B, giving polarized and depolarized Raman bands, respectively. Since BCC has no symmetry elements, all the vibrational bands belong to the same species.

No description of the approximate motions involved in the fundamental vibrations has been attempted. These modes are undoubtedly highly mixed in the *trans*-1,2-dihalocyclohexanes because of the low symmetry, and the assignments for cyclohexane [28-29] (D_{3d} symmetry) would be of limited aid. Some comments will be made concerning the fundamentals around $500-800$ cm^{-1} and around 1000 cm^{-1}.

Various intense infrared and Raman bands are observed in the region $800-500$ cm^{-1} which undoubtedly involve the C$-$Hal stretching vibrations to a considerable extent. Various dihalogenated cyclohexane derivatives with vicinal *trans* configuration have been studied by spectroscopic technique by Altona, Hageman and Havinga.[18,30] They offer very convincing arguments for their assignments of the C$-$X stretching modes in these molecules, which differ from those originally suggested [6,8] by a larger separation of the symmetrical and asymmetrical *aa* C$-$X stretching modes. Their attributions are adopted in Table 4 and give a regular correlation between the present molecules as well as for *trans*-1,2-chloroiodocyclohexane [16] giving: *ee*, 738 and 655, and *aa*, 640 and 557 cm^{-1}. However, comparison with the monohalocyclohexanes,[7,15] *trans*-1,4-dihalocyclohexanes,[31,32] and various tetrahalocyclohexanes [32] as well as the monohalocyclopentanes [33] give widely different values for the "C$-$Hal stretching vibrations". A considerable mixing between the C$-$Hal stretching vibrations and skeletal stretching as well as methylene rocking modes seems present, and might be verified by force constant calculations.

It appears from Tables 1 — 4 that two strong infrared bands with weaker Raman counterparts were observed around 1000 cm^{-1} for each of the present molecules. At slightly higher frequencies another pair was observed which was more intense in the Raman spectrum. Two corresponding pairs of bands were observed for the monohalocyclohexanes [7,15] and trans-1,4-dihalocyclohexanes,[31,32] and they are listed in Table 5. Only in the case of monochloro-

Table 5. Some characteristic skeletal vibrations in halogeneted cyclohexanes.

Compound	Substituent	a (aa)		e (ee)		$\Delta \nu^a$
		IR	Raman	IR	Raman	
Monohalocyclohexane^b	Cl	1029 m	1028 vs	1029 m	1028 vs	0
		1014 s	1013 w	993 vs	993 s	21
	Br	1028 w	1028 s	1028 w	1028 s	0
		1010 m	1010 w	988 s	989 s	22
	I	1021 w	1023 s	1030 m	1032 s	−9
		1006 s	1008 vw	988 vs	988 s	18
	Cl Cl	1050 m	1051 s	1032 m	1033 m	18
trans-1,2-Dihalo-		1005 vs	1006 vw	980 vs	981 s	25
cyclohexane	Cl Br	1048 m	1049 s	1032 s	1035 s	16
		1000 s	1001 m	976 s	976 s	24
	Cl I^c	1031 m	1032 s	1046 w	1047 s	15
		996 vs	997 m	973 vs	974 s	23
	Br Br	1032 s	1032 s	1047 m	1047 s	15
		999 vs	999 w	972 s	971 m	27
trans-1,4-Dihalo-	Cl Cl	—	1029 s	—	1006 s	23
cyclohexane ^{d,e}		1003	—	988	—	15
		—		—		
	Br Br	—	1028 s	—	999 s	29
		1004	—	989	—	15

^{a} Calculated from IR frequencies of the liquids when possible. ^{b} Ref. 15. ^{c} Ref. 16. ^{d} Ref. 31. ^{e} Ref. 32.

and monobromocyclohexane does the higher frequency pair coincide to one band at 1028 cm^{-1} common to both conformers.[15] These vibrational bands have previously been assigned [8,15,31] as ring stretching modes for the halogenated cyclohexanes. A doubly degenerate e_g mode has been observed in cyclohexane [28] at 1026 cm^{-1} and assigned [28,29] as a ring strecthing vibration. For cis-1,2-dichlorocyclohexane,[8] having only one conformation, the bands at 1025 and 986 cm^{-1} correspond to the two pairs of bands, respectively. The constant position and high intensities of these bands in the infrared and in Raman make them very significant for diagnostic purpose. Various other halogenated cyclohexanes are presently being studied and correlated with the present data.

REFERENCES

1. Hassel, O. *Research* **3** (1950) 504.
2. Eliel, E. L., Allinger, N. L., Angyal, S. J. and Morrison, G. A. *Conformational Analysis*, Interscience, New York 1966.
3. Hanack, M. *Conformational Theory*, Academic, New York 1965.
4. Kohlrausch, K. W. F. and Stockmair, W. *Z. physik. Chem.* **31** (1936) 382.
5. Larnaudie, J. M. *Compt. Rend.* **235** (1952) 154; **236** (1953) 919.
6. Kozima, K., Sakashati, S. and Maeda, S. *J. Am. Chem. Soc.* **76** (1954) 1965.
7. Klæboe, P., Lothe, J. J. and Lunde, K. *Acta Chem. Scand.* **10** (1956) 1465.
8. Klæboe, P., Lothe, J. J. and Lunde, K. *Acta Chem. Scand.* **11** (1957) 1677.
9. Tulinskie, A., Giacomo, A. and Smyth, C. P. *J. Am. Chem. Soc.* **75** (1953) 3552.
10. Kwestroo, W., Meijer, F. A. and Havinga, E. *Rec. Trav. Chim.* **T 73** (1954) 717.
11. Bender, P., Flowers, D. and Goehring, H. L. *J. Am. Chem. Soc.* **77** (1955) 3463.
12. Hageman, H. J. and Havinga, E. *Rec. Trav. Chim.* **88** (1969) 97.
13. Whatley, L. S., Lippincott, E. R., Valkenburg, A. V. and Weir, C. E. *Science* **144** (1964) 968.
14. Brasch, J. W. *J. Chem. Phys.* **43** (1965) 3473.
15. Klæboe, P. *Acta Chem. Scand.* **23** (1969) 2641.
16. Thorbjørnsrud, J. and Klæboe, P. *Acta Chem. Scand.* **25** (1971) 781.
17. Mousseron, M., Granger, R. and Valette, J. *Bull. Soc. Chim. France* **1946** 244.
18. Altona, C., Hageman, H. J. and Havinga, E. *Spectrochim. Acta* **A 24** (1968) 633.
19. Dempster, A. B., Price, K. and Sheppard, N. *Spectrochim. Acta* **A 25** (1969) 1381.
20. Thorbjørnsrud, J., Klæboe, P. and Ellestad, O. H. *To be published.*
21. Powling, J. and Bernstein, H. J. *J. Am. Chem. Soc.* **73** (1951) 1815.
22. Hageman, H. J. and Havinga, E. *Tetrahedron Letters* **22** (1966) 2271.
23. Rogers, M. T. and Canon, M. J. *J. Phys. Chem.* **65** (1961) 1417.
24. Reeves, L. W. and Strømme, K. O. *Trans. Faraday Soc.* **57** (1961) 390.
25. Pentin, Y. A., Kuz'yants, G. M. and Ul'yanova, O. D. *Zh. Fiz. Khim.* **38** (1964) 1302; *Russ. J. Phys. Chem.* **38** (1964) 708.
26. Brasch, J. W. and Jakobsen, R. J. *Spectrochim. Acta* **21** (1965) 1183.
27. Bastiansen, O., Hassel, O. and Munthe-Kaas, A. *Acta Chem. Scand.* **8** (1954) 872.
28. Miller, F. A. and Golob, H. R. *Spectrochim. Acta* **20** (1964) 1517.
29. Takahashi, H., Shimanouchi, T., Fukushima, K. and Miyazawa, T. *J. Mol. Spectry.* **13** (1964) 43.
30. Altona, C. *Tetrahedron Letters* **19** (1968) 2325.
31. Kozima, K. and Yoshino, T. *J. Am. Chem. Soc.* **75** (1953) 166.
32. Klæboe, P. *To be published.*
33. Ekejiuba, I. O. C. and Hallam, H. E. *Spectrochim. Acta* **A 26** (1970) 59,67.

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