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Spectroscopic Studies of 1,1-Dichloro-, *cis*-1,4-Dichloro-, and *cis*-1-Bromo-2-chlorocyclohexane

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The IR spectra of the three title compounds as liquids, in the solid state at −70 or −180 °C and at ambient temperature under high pressure were recorded in the region 4000 – 200 cm^{-1}. Correspondingly, Raman spectra of the liquids, including semi-quantitative polarization measurements of the dichloro compounds, and spectra of the low temperature solids were recorded.

The spectra of 1,1-dichloro- and *cis*-1,4-dichlorocyclohexane were interpreted in terms of C_s symmetry; the fundamentals were assigned and compared with those of *trans*-1,4-dichlorocyclohexane.

cis-1-Bromo-2-chlorocyclohexane consisted of two conformers (Br(*e*), Cl(*a*) and Br(*a*), Cl(*e*) in the liquid state (at low temperature and under high pressure). Presumably, the two conformers can be simultaneously present in a 1:1 ratio in the crystallographic unit cell.

As a continuation of our spectral studies of halogenated cyclohexanes,[1] we have now investigated 1,1-dichloro-, *cis*-1,4-dichloro-, and *cis*-1-bromo-2-chlorocyclohexane, later to be called 1,1-DCC, 1,4-DCC, and 1,2-BCC, respectively, in this paper. Obviously, 1,1-DCC and 1,4-DCC are transferred into their mirror images upon conversion of the cyclohexane ring, leading to spectra of one single conformation. It was our goal to interpret the IR and Raman spectra of these compounds and compare them with those of related molecules, notably chlorocyclohexane [2–4] and *trans*-1,4-dichlorohexane.[5] Later, we intend to derive force fields for the chlorinated cyclohexanes, partly transferred from the thorough work recently published for cyclohexane itself.[6]

The third compound 1,2-BCC was expected to give more complicated spectra because of the non-identical conformers. These are distinguished by an interchange of the two halogens, Br(*e*), Cl(*a*) and Br(*a*), Cl(*e*), thought to be of nearly equal abundance. We have previously studied the crystalline solids of various *trans*-1,2-dihalocyclohexanes [1,7] (dichloro, dibromo, 1-chloro-2-bromo, 1-chloro-2-iodo, and 1-bromo-2-iodo), revealing a preference for the *aa* conformer with bulky halogens. In 1,2-BCC we wanted particularly to decide which of the two very similar conformers existed in the crystalline state.

EXPERIMENTAL

The sample of 1,1-DCC was prepared from cyclohexanone and phosphorus pentachloride, and was steam distilled, dried and purified by repeated fractional distillation (b.p. 172 °C, n_D (20 °C) 1.4790) according to well known methods.[8] 1,4-DCC was prepared by reacting 1,4-cyclohexandiol with HCl, and separated from the *trans* compound by fractional crystallization.[9] The sample was purified by distillation and subsequent preparative gas liquid chromatography (m.p. 18 °C, n_D (20 °C) 1.4942) and the NMR spectrum found identical with that reported.[10] The sample of 1,2-BCC was prepared by adding hypobromous acid to cyclohexene giving *trans*-2-bromocyclohexanol. This material reacted with thionylchloride in the presence of pyridine. Since this reaction proceeds with inversion [8,11] 1,2-BCC was formed, and separated from the less volatile *trans*-1-bromo-2-chlorocyclohexane by distillation under reduced pressure in a column having 30 theoretical plates. After three times fractionation the sample was better than 99 % pure as checked by gas chromatography (n_D (20 °C) = 1.4982).

The IR and Raman spectrometers, cryostats,

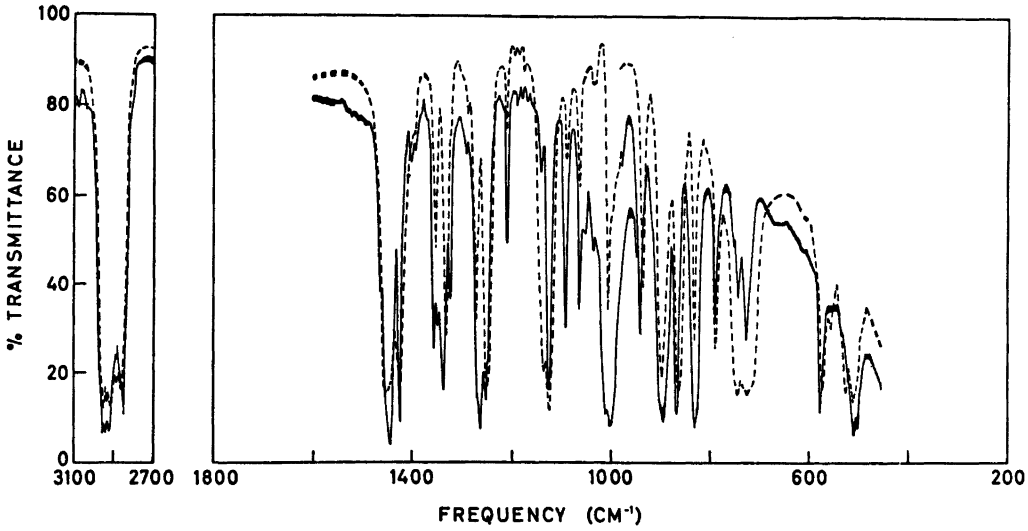

Fig. 1. The IR spectrum of a single crystal of 1,1-dichlorocyclohexane (20 kbar, 50 °C), using planar polarized radiation.

high pressure diamond cell, and general experimental procedure have been described in detail elsewhere.[4,5,7]

RESULTS AND DISCUSSION

With 18 atoms in the molecule 1,1-DCC and 1,4-DCC should have 48 fundamentals whereas 1,2 BCC should have still richer IR and Raman spectra because of the simultaneous presence of two conformers with non-identical vibrational modes. The spectral results were in good agreement with these predictions as seen from Tables 1 (1,1-DCC), 2 (1,4-DCC), and 4 (1,2-DBC). As an illustration of our high pressure technique,[7] the high pressure crystalline solids of the three compounds are given in Figs. 1, 2 and 3, respectively. For 1,1-DCC, a single crystal was prepared and an IR spectrum revealing the dichroism is shown in Fig. 1.

Obviously, 1,1-DCC as well as 1,4-DCC both belong to point group C_s and the 48 fundamentals divide themselves between 27 A' and 21 A''. The IR vapour contours were poorly resolved and therefore not useful for classifying the vibrations into the symmetry species. However, like other chlorinated or brominated cyclohexanes [1,5,7] the present compounds had intense Raman spectra and most of the fundamentals could be assigned with reasonable confidence from the polarization measurements. The resemblance with cyclohexane,[6] chlorocyclohexane,[2-4] and *trans*-1,2-dichlorocyclohexane [1,7] was of considerable help for the interpretations. Most of all, the striking similarity between the spectra of 1,1-DCC and 1,4-DCC with *trans*-1,4-dichlorocyclohexane was of special significance because of the very complete data recently obtained [5] for the latter molecule.

1,1-Dichlorocyclohexane. Our tentative assignments for this molecule are given in Table 1 and for the sake of brevity only some very short comments will be given. The 10 C–H stretching modes (6 $A'+4\,A''$) partly coincided into out-of-phase (above 2900 cm^{-1}) and in-phase (below 2900 cm^{-1}) CH_2 stretches, making the interpretations somewhat ambiguous. Five CH_2 scissoring modes (3 $A'+2\,A''$) were assigned around 1420 cm^{-1} of which ν_9 and ν_{23} presumably overlapped. The corresponding CH_2 wagging modes were found between 1350 and 1250 cm^{-1}. Below, vibrations classified as CH_2 twisting (5) and rocking (5) mixed with six ring stretching modes were observed between 1250 and 530 cm^{-1}.

Particular interest is focused on the C–Cl stretching frequencies since these modes are generally regarded as group frequencies, sensitive to conformational changes in open chain and cyclic compounds.[12] In 1,1-DCC the C–Cl

Table 1. Infrared and Raman spectral data[a] of 1,1-dichlorocyclohexane.

Liquid IR	Raman		Solid Pressure 20 kbar IR		Assignments	
2950 s,sd[b]	2953 m,sd	P	2945 vs[c]		A'	ν_1
2940 s,sd	2941 s	P			A',A''	ν_2, ν_{28}
2920 s,sd	2918 m	D	2920 vs		A',A''	ν_3,ν_{29}
2899 m	2903 m	P	2900 m		A'	ν_4
2860 s	2862 m	P	2862 s		A',A''	ν_5, ν_{30}
2844 m,sd	2842 w	P	2845 m,sd		A',A''	ν_6,ν_{31}
1460 m	1459 w	P?	1462 m		A'	ν_7
1448 s	1449 vs[d]		1449 s		A''	ν_{32}
1444 s,sd	1442 s[d]		1441 s	∥	A'	ν_8
1427 m	1428 m	D	1422 s	∥	A',A''	ν_9, ν_{33}
1397 vw			1399 w	∥		$\nu_{23}+\nu_{41}$
1353 m	1352 w	P	1352 s	⊥	A'	ν_{10}
1345 m,sd	1347 w,sd	D	1347 m	∥	A''	ν_{34}
1336 m	1336 m	P	1333 s		A'	ν_{12}
1317 w	1319 w	D	1322 w	∥	A''	ν_{35}
1268 m	1267 s	P	1269 s	∥	A'	ν_{12}
1260 m,sd			1260 m,sd			$\nu_{23}+\nu_{44}$
1246 s	1247 w	P	1249 vs	∥	A'	ν_{13}
1205 vw	1205 w	D	1209 m	∥	A''	ν_{36}
1136 m	1136 w	P?	1138 m	⊥	A'	ν_{14}
1124 s	1124 m	D	1123 s	⊥	A''	ν_{37}
1082 w	1082 w	D?	1087 m	∥	A''	ν_{38}
1067 vw	1066 m	D	1062 m	∥	A''	ν_{39}
1044 vw	1045 vw		1048 w	∥		$\nu_{21}+\nu_{22}$
1027 w	1027 s	D	1030 m		A''	ν_{40}
1018 w,sd			1018 w,s[d]	∥		$\nu_{22}+\nu_{23}$
1004 vs	1004 s	P	1005 s	∥	A'	ν_{15}
944 vw			945 w,sd			$\nu_{20}+\nu_{46}$
929 w	929 vw		934 m			$\nu_{21}+\nu_{45}$
897 m,sd	897 w,sd	D	896 m,sd[d]		A''	ν_{41}
890 s	890 s	D	889 vs[d]	∥	A''	ν_{42}
864 s	864 s	P	863 vs		A'	ν_{16}
825 s	825 vs	P	829 s	∥	A'	ν_{17}
820 s	820 m,sd	D	819 w,sd		A''	ν_{43}
779 w	781 w	D	784 s	⊥	A''	ν_{44}
766 w,bd			772 w,sd			$\nu_{23}+\nu_{26}$
737 vs	737 m	P	739 s	⊥	A'	ν_{18}
720 vs	721 s	P	722 s	⊥	A'	ν_{19}
570 s	572 vs	P	572 vs	∥	A'	ν_{20}
535 w,sd	535 w	P?	545 w		A'	ν_{21}
521 s	522 s	P	521 s	⊥	A'	ν_{22}
500 s	502 vs	P	503 vs	∥	A'	ν_{23}
460 w	458 w	P	460 w			$2\,\nu_{47}$
389 w	389 w	D?	394 w		A''	ν_{45}
374 m	375 s	D	382 m		A''	ν_{46}
354 m	354 vs	P	355 s		A'	ν_{24}
302 m	303 s	P	310 m		A'	ν_{25}
267 s	270 vs	P	272 s		A'	ν_{26}
234 w	234 w	D	243 w		A''	ν_{47}
207 w	209 vs	P	215 m		A'	ν_{27}
	179 m	D			A''	ν_{48}

[a] Very weak bands in the region 4000–3000 and 2700–1500 cm^{-1} were omitted. [b] Abbreviations: s, strong; m, medium; w, weak; v, very; sd, shoulder, bd, broad, P, polarized; D, depolarized; ∥ and ⊥, dichroic measurements. [c] Intensities obtained by ordinary infrared radiation, contrary to Fig. 1. [d] Bands observed at −170 °C.

Table 2. Infrared and Raman spectral data [a] of *cis*-1,4-dichlorocyclohexane.

Liquid IR	Raman		Solid (−70 °C) IR	Assignment
2956 vs[b]	2961 s	D	2977 s	A'' ν_{28}
			2938 s	A', A' ν_1,ν_2
2912 s	2910 s	P	2911 vs	A', A'' ν_3,ν_4,ν_{29}
2869 s	2872 s	P	2870 s	A',A'' ν_5,ν_{30}
2846 s	2845 s	P	2846 m	A', A'' ν_6,ν_{31}
1460 s	1460 m	D?		
1457 s,sd	1456 m,sd		1458 s	A' ν_7
1442 vs	1442 s	D	1442 s	A'' ν_{32}
1437 s,sd	1434 s	P	1435 s	A' ν_8
1430 s	1430 m	D	1426 m,sd	A'' ν_{33}
1358 m	1356 s	P	1358 s	A' ν_9
1351 s,sd	1349 s	P	1351 s	A' ν_{10}
1345 s	1345 m	D	1347 s	A'' ν_{34}
1318 w	1320 w	D	1318 w	A'' ν_{35}
1301 vw	1300 w		1300 w	$\nu_{17}+\nu_{46}$
1290 vw	1290 w	P?	1290 w	$\nu_{17}+\nu_{24}$
1276 vs	1276 s	P	1277 s	A' ν_{11}
1265 s	1266 m	D?	1266 s	A'' ν_{36}
1238 s	1238 m	P	1238 s	A' ν_{12}
1218 w,sd	1216 w	P	1218 w	$\nu_{18}+\nu_{24}$
1191 s	1191 m	D	1188 s	A'' ν_{37}
1141 m	1141 m	P	1142 m	A' ν_{13}
1121 w	1121 w	D	1121 w	A'' ν_{38}
1095 vw	1096 vw	P	1095 w	A' ν_{14}
1080 m	1081 m	D	1080 s	A'' ν_{39}
1075 m	1076 m	D	1074 s	A'' ν_{40}
1054 w,sd	1055 w,sd	P	1054, w,sd	A' ν_{15}
1024 m	1024 s	D	1024 s	A'' ν_{41}
995 vs	997 s	P	996 s	A' ν_{16}
972 m,sd	970 w	P?	972 m,sd	A' ν_{17}
955 vw			953 vw	$\nu_{23}+\nu_{45}$
932 m	930 m	D	935 vw	A'' ν_{42}
897 s			899 m	A' ν_{18}
876 vs	876 m	D	875 s	A'' ν_{43}
839 w,sd			838 w	$\nu_{23}+\nu_{25}$
827 vs	828 s	P	827 s	A' ν_{19}
805 w			806 w	$\nu_{21}+\nu_{48}$
780 m	775 vs	P	778 s	A' ν_{20}
771 s	771 m,sd		765 s	A'' ν_{44}
756 w,sd	756 w,sd		756 m	$\nu_{23}+\nu_{27}$
715 m	714 s	P	715 w	A' ν_{21}
683 vs	685 s	P	680 s	A' ν_{22}
661 w,sd	662 vw	D?	660 m	$\nu_{24}+\nu_{26}$
588 w,sd	590 w,sd	P	590 w	$2\ \nu_{25}$
566 s	566 vs	P	560 s	A' ν_{33}
470 w	467 w	D	470 w	$\nu_{26}+\nu_{47}$
438 w	437 w	D	439 w	$\nu_{27}+\nu_{47}$
390 m	390 vs	D	385 s	A'' ν_{45}
350 w,sd			348 w	$\nu_{47}+\nu_{48}$
341 m	341 m	D	341 m	A'' ν_{46}
326 s	325 vs	P	326 s	A' ν_{24}
301 vw	300 w,sd	P	302 w	A' ν_{25}
277 vw	279 w	D	278	$\nu_{27}+\nu_{48}$
257 m	257 s	D	261 m	A'' ν_{47}
212 m	213 m	P	216 m	A' ν_{26}
	197 m	P		A' ν_{27}
	94 vs	D		A'' ν_{48}

[a] Very weak bands in the regions 4000–3000 and 2700–1500 cm^{-1} were omitted. [b] For abbreviations, see footnotes to Table 1.

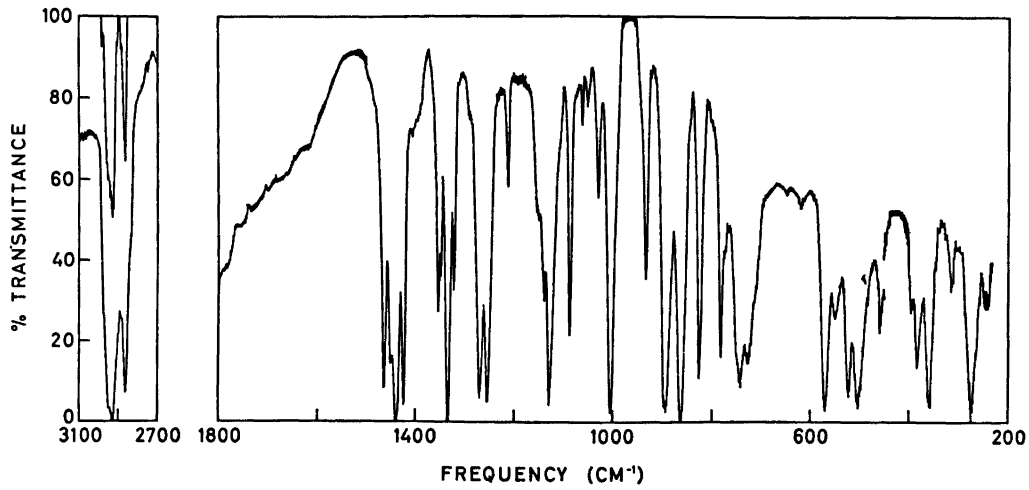

Fig. 2. The IR spectrum of polycrystalline *cis*-1,4-dichlorocyclohexane (20 kbar, 50 °C).

stretching frequencies were tentatively attributed to the intense bands at 737 and 720 cm^{-1}, although the small separation between them seemed surprising. Thus, in the related 2,2-dichloropropane the geminal C–Cl stretching modes were found [13] at 669 and 562 cm^{-1}, suggesting the 570 cm^{-1} band as another possible choice in 1,1-DCC. As apparent from Table 3, however, no C–Cl stretch as low as 570 cm^{-1} has to our knowledge been suggested in cyclohexanes. This leaves us with the 737 and 720 cm^{-1} bands supporting the notion that more than one chlorine on a carbon raises the C–Cl stretching frequency.[14]

Ten additional fundamentals (6 $A'+4$ A'') connected with ring bend and CCX bends are expected, and as apparent from Table 1 they fit nicely in with the experimental data. Only a few weak IR and Raman bands were not assigned as fundamentals and they can easily be interpreted as binary combination bands.

As apparent from Fig. 1 and Table 1, the dichroic ratios (symbolized with $\parallel$ and $\perp$ in Table 1) bear no simple correlation to the symmetry species A' and A''. In order to derive this relationship the orientation of the high pressure single crystal in the diamond cell and the crystallographic space group should be known.

cis-*1,4-Dichlorocyclohexane.* We expect mostly the same number of fundamentals in the respective regions for 1,4-DCC as for 1,1-DCC. The structural differences: four methylene and two methine groups (1,4-DCC) contra five methylene groups (1,1-DCC) will result in slight differences in the various CH_2 stretching and bending

Table 3. Carbon-chlorine stretching vibrations in cyclohexanes.

Compound	Equatorial	Axial
Chlorocyclohexane [a]	731	684
1,1-Dichlorocyclohexane [b]	737	720
cis-1,4-Dichlorocyclohexane [b]	780	683
trans-1,4-Dichlorocyclohexane [c]	782	756
	726	648
trans-1,2-Dichlorocyclohexane [d]	743	695
	736	616

[a] Ref. 4. [b] This work. [c] Ref. 5. [d] Refs. 7 and 12.

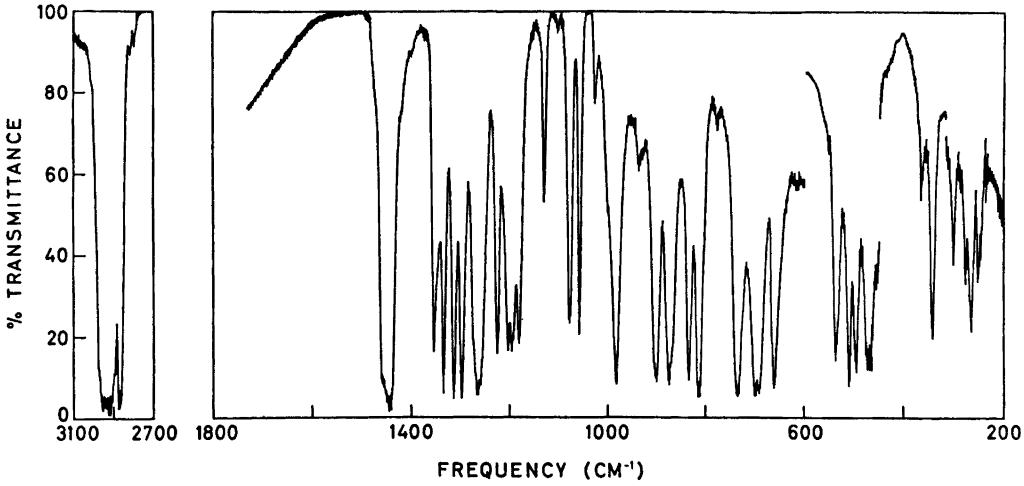

Fig. 3. The IR spectrum of polycrystalline *cis*-1-bromo-2-chlorocyclohexane at ambient temperature (*ca.* 20 kbar pressure).

regions. Also the widely separated heavy chlorine atoms will lead to considerably lower CCCl bending frequencies in 1,4-DCC compared to 1,1-DCC.

The 10 C–H stretching vibrations overlapped considerably as found for cyclohexanes,[5,6] 1,4-dioxan and related compounds.[15] As apparent from Table 2, the various methylene and C–H deformation frequencies appear in the expected regions below 1500 cm^{-1}. The intense bands at 1024 and 995 cm^{-1} in 1,4-DCC (1027 and 1004 cm^{-1} for 1,1-DCC) previously [7] considered as ring stretching modes have diagnostic value for evaluating conformational equilibria in halogenated cyclohexanes.

The bands at 780 and 683 cm^{-1} were interpreted as the C–Cl stretching modes, the former very intense in Raman, the latter in IR. The fundamentals assigned to the "C–Cl stretching modes" (undoubtedly mixed with C–C stretch and CH_2 deformations) for various chlorinated cyclohexanes are shown in Table 3.

Ten additional fundamentals (6 $A'+4$ A'') mainly involving ring bend and CCCl bend were expected below the C–Cl stretching modes and were assigned to distinct IR and Raman bands. The lowest vibrational modes were found at 257, 212, 197 and 94 cm^{-1} in good agreement with the results for *trans*-1,4-dichlorocyclohexane.

cis-*1-Bromo-2-chlorocyclohexane.* Like the other dihalocyclohexanes 1,2-BCC should have approximately 34 fundamentals (CH_2 stretch and scissor excluded) below 1400 cm^{-1} for each conformer. From the IR and Raman frequencies (Table 4) it can be seen that close to 50 bands were observed in this region. Although some of the lines in BCC can be combination bands or overtones the data clearly demonstrate that both conformers Br(*e*), Cl(*a*) and Br(*a*), Cl(*e*) were present. Moreover, the IR and Raman spectra of 1,2-BCC are very similar to those of the *trans*-1,2-dihalocyclohexane [7] and to *trans*-1-bromo-2-chlorocyclohexane [7,16] in particular. This compound had a few additional bands compared to 1,2-BCC which can be explained as additional cases of overlapping bands belonging to both conformers in the latter spectra. It is actually surprising that the two conformers of 1,2-BCC, considering their similarity, have so comparatively few coinciding conformer bands.

As apparent from Table 4 the low temperature IR and Raman spectra of solid 1,2-BCC were practically identical to those of the liquid. No significant cases of bands vanishing in the solid were observed, in spite of several attempts in various cryostats and prolonged annealing just below the melting point. Since we would expect only one conformer in crystalline 1,2-BCC like in other halogenated cyclohexanes, it seemed possible that the low temperature solid was

Table 4. Infrared and Raman spectral data of *cis*-1-bromo-2-chlorocyclohexane.

Liquid IR[a]	Raman	Solid IR High press. (*ca.* 20 kbar)	Low temp [a] (−70 °C)	Raman Low temp (−170 °C)
				2987 w
2959 m[b]	2957 m		2959 m	2955 s
2944 vs	2945 s	2940 vs, bd	2944 vs	2945 vs
	2911 m			2921 m
2902 m,sd	2903 s		2901 m,sd	2903 s
2871 vs			2872 vs	
	2866 s	2867 vs		2860 s
2863 vs			2863 vs	
2850 m,sd	2849 m		2850 m,sd	
1460 s	1458 w,sd	1460 m,sd	1460 s	1457 w
1448 vs	1446 s		1443 vs	1442 m
		1441 vs		
1436 s	1436 m		1434 s	
1356 m	1355 m,sd	1353 m	1356 m	
1346 m	1345 m	1346 m,sd	1346 m	1347 m,sd
1335 m	1334 m	1332 s	1334 s	1336 m
1311 s	1311 m	1311 s	1313 s	1311 m
1298 s	1297 m	1298 s	1297 s	1301 m
1272 s	1271 m	1272 s,bd	1272 m	1275 m
1268 m,sd			1268 m,sd	
1263 vs	1262 s	1260 s	1261 s	1260 s
1224 m	1224 m	1223 s	1224 s	
1203 s	1203 m	1204 s	1204 s	
1196 s	1195 m	1194 s	1195 s	1193 m
1190 w,sd			1191 m,sd	
1180 s	1183 m	1179 s	1181 s	1182 w
1130 m	1131 w	1129 m	1129 s	1130 s
1103 vw		1102 w	1101 w	
1080 m	1080 m	1079 m	1080 m	1082 m
1076 m	1077 m,sd	1074 m	1075 m	1077 w
1056 w	1056 m	1058 m	1057 m	1058 m
			1054 w	
1025 w	1025 m	1027 m	1027 w	1027 m
984 vs	982 s	982 vs	986 vs	986 vs
980 m,sd			981 m	981 m
935 vw	935 vw	938 w	935 w	
904 s	906 m		906 s	908 w
899 m,sd	899 m	901 s	899 s	899 w
877 s	875 s	877 s	877 s	877 vs
870 s	869 s	871 s	871 s	870 s,sd
832 s	832 s	833 s	832 s	834 s
816 s	815 m	817 m	815 s	811 m
809 m	810 m	811 m,sd	810 m	807 w
780 vw		778 w	782 w	
763 vw			761 w	
740 s	739 s	737 s	739 s	732 s
701 s	700 vs	701 s	701 s	698 vs
697 s	694 vs	693 s	694 s	693 s
662 s	662 vs	662 s	662 s	659 s
648 w,sd			647 w	
539 s	539 s	537 s	537 s	532 s
510 m	509 vs	510 s	509 s	509 m
496 m	496 s	496 s	495 m	495 m
473 s	472 s	470 s,bd	473 s	468 vs
465 m,sd			465 m,sd	

Table 4. Continued.

392 vw			390 vw	
369 w	368 w,sd	390 vw	364 w	368 w,sd
		365 m		
357 m	358 m		357 w,sd	359 m
342 s	343 vs	343 s	342 s	341 s
				310 m,sd
299 m	300 s	300 m	299 m	300 s
275 s	276 m,sd	277 m	276 s	279 w
264 s	265 vs	265 s	263 s	264 vs
247 m	248 s	250 m	248 m	244 s
	182 m			180 m
	179 m			174 m
	152 m,sd			
	143 s			147 s
	114 s			118 s
				104 w

[a] Very weak IR bands in the regions 4000 – 3000 cm^{-1} and 2700 – 1500 cm^{-1} are omitted. [b] For abbreviations, see footnotes to Table 1.

amorphous and not truly crystalline. However, the IR and Raman bands were narrow and "looked" crystalline although only few cases of correlation splitting were observed.

The IR spectrum of the high pressure crystal of BCC is shown in Fig. 3. From this curve as well as from the frequencies of Table 3 it can be concluded that no liquid IR bands vanished in the high pressure solid either. Because of the small sample size and low IR signal, large slits were employed in the high pressure recordings and close bands were not always resolved. It is highly significant, however, that the crystallinity of the high pressure solid was ascertained by visual observation in a polarization microscope. Therefore it has to be concluded that the high pressure (probably also the low temperature) crystals contained both conformers. Presumably, the extreme similarity of the conformers in 1,2-BCC makes a mixed crystal consisting of Br(*e*), Cl(*a*) and Br(*a*), Cl(*e*) feasible.

No variations in relative band intensities between the liquid, low temperature or high pressure solids were observed. Moreover, separate recordings of the liquid spectra at −10, 30 and 100 °C did not reveal any relative intensity variations with temperature, indicating a negligible enthalpy difference (ΔH) between the conformers. This is entirely as expected when assuming additive contributions from bromo- and chloro-cyclohexane each having practically the same ΔG values.[17] Therefore, nearly equal concentrations of each conformer seem present in the solids as well as in liquid 1,2-BCC. If the low temperature and high pressure crystals consist of molecules of Br(*a*), Cl(*e*) and Br(*e*), Cl(*a*) conformers of 1:1 ratio in the crystal lattice or if a solid solution of the two conformers are present, cannot be decided.

Both conformations of 1,2-BCC have C_1 symmetry and the vibrational bands therefore all belong to the same symmetry species. Accordingly no information can be extracted from IR vapour band contours or Raman polarization measurements. The spectral region around 1000 cm^{-1} was not as straightforward as for other halogenated cyclohexanes.[5,7] Two bands at 1025 and 984 cm^{-1} can possibly be assigned to one of the conformers and those at 1056 and 980 cm^{-1} to the other, corresponding to 1032 and 1000 cm^{-1} (*aa*) and 1048 and 976 cm^{-1} (*ee*) in *trans*-1-bromo-2-chlorocyclohexane.[7] The close spacing between the bands at 984 and 980 cm^{-1} in 1,2-BCC contrasts the *trans*-1,2-dihalocyclohexanes where the spacing is approximately 25 cm^{-1}.[7]

Extensive studies of the C–hal stretching vibrations in open chains have been reported[11] and successfully applied to cyclohexanes by Altona *et al.*[12] The atom situated *anti* to the halogen influences the C–hal stretching frequency significantly, resulting in equatorial halogens having higher stretching frequencies than axial. Applying suggested values for these frequencies in cyclohexanes,[11,12] the following frequencies were derived: 742 and 660 cm^{-1} for

Br(*a*) Cl(*e*) and 686 and 685 cm*a*[1] for Br(*e*) Cl(*a*). As apparent from Table 4, four bands of high intensity in IR as well as in Raman were observed at 740, 701, 697, and 662 cm^{-1} presumably connected with the C–hal stretching modes. Accordingly, these frequencies can tentatively be assigned as the C–Cl(*e*), C–Br(*e*), C–Cl(*a*), and C–Br(*a*) stretches, respectively, the high and low frequency bands belonging to conformer Br(*a*), Cl(*e*) and the doublet at 701 and 697 cm^{-1} belonging to Br(*e*), Cl(*a*). The extremely close spacing of the doublet ($\Delta\nu \sim 5$ cm^{-1}) is very surprising for two fundamentals of the same molecule and might suggest very little vibrational interaction between the two stretching movements.

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