THE CONFORMATION AND VIBRATIONAL SPECTRA OF *trans*-1,4-DIHALOCYCLOHEXANES

Part III. trans-1,4-Diiodo-, trans-1,4-bromoiodo- and trans-1,4-dibromocyclohexane

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ABSTRACT

The IR spectra of *trans*-1,4-diiodo- and *trans*-1,4-bromoiodocyclohexane as solutes in various solvents, as pellets and as solids under high pressure are recorded in the region $4000-30 \text{ cm}^{-1}$. Additional spectra of the melts, amorphous and annealed crystalline solids at 90 K and dichroic spectra of oriented crystals are recorded above 200 cm⁻¹. Raman spectra of the amorphous and annealed solids at 90 K and as solutes in various solvents, are obtained, including polarization measurements. IR and Raman spectra of *trans*-1,4-dibromocyclohexane in the temperature range 90-250 K are recorded. Equilibrium mixtures of ee and aa conformers of the title compounds are observed in solution, in the melts and in the amorphous solid at 90 K. The ee conformer only is present in the stable crystal, while the aa conformer predominates in apparently metastable crystals annealed to ca. 205 K. The concentration of the aa conformer increases under high pressure (50 kbar). Fundamental frequencies for both ee and aa conformers are assigned. A normal coordinate analysis is carried out, and the force fields adjusted to nine halogenated cyclohexanes using the overlay technique.

INTRODUCTION

In previous papers in this series [1, 2] we have reported the conformations and vibrational spectra of the two symmetric molecules *trans*-1,4-dichloro-(DCC) and *trans*-1,4-dibromocyclohexane (DBC), as well as those of the asymmetric molecules *trans*-1,4-chlorobromo- (CBC) and *trans*-1,4-chloroiodocyclohexane (CIC). The two remaining members of the series, *trans*-1,4-diiodo-(DIC) [3] and *trans*-1,4-bromoiodocyclohexane (BIC), will be considered in the present contribution.

It was observed that DBC, when annealed carefully to temperatures in the range 160-205 K, contained practically pure as conformer, contrary to our earlier results [1]. These new IR and Raman data are included in the present paper.

The conformational and spectral features of the compounds DIC, BIC and DBC are very similar to those of DCC [1], CBC and CIC [2]. Since the con-

formational changes taking place in the solids with variation in temperature or pressure have already been described in considerable detail [1, 2], these effects will be mentioned only briefly.

EXPERIMENTAL

DIC was prepared by treating 1,4-cyclohexanediol (Merck) with HI, and was subsequently purified by successive sublimations in vacuo (m.p. 142°C). 1,4-Bromohydroxycyclohexane was prepared from 1,4-cyclohexanediol by reaction with hydrobromic acid and purified by distillation. Treatment with phosphorus triiodide gave BIC in good yield, in analogy with the syntheses of CBC and CIC [2]. The product was recrystallized twice from ligroin and sublimed in vacuo (m.p. 124°C).

The sample of DIC was very pure, while some small impurities (DBC and DIC) were present in the sample of BIC, appearing as weak bands in the IR and Raman spectra. We were not able to completely remove these impurities by recrystallization, as was also the case for the other asymmetric compounds, CBC and CIC [2]. However, since the spectra of the impurities are well known, the presence of these compounds did not severely affect the interpretation.

When BIC was stored at 0° C, unidentified impurities (not DBC or DIC) appeared after several weeks. A freshly prepared sample of BIC was therefore used in all important experiments. The sample of DBC, left over from our earlier study [1], was repurified by sublimation.

The spectrometers (dispersive and Fourier-transform IR spectrometers and a Raman spectrometer) have already been described [2]. Raman spectra of BIC were also recorded on a Coderg T 800 spectrometer, using a Spectra Physics argon ion laser at the University of Tübingen, G.F.R.

The experimental techniques utilised, including heating the solids to their melting point and subsequently cooling them under a temperature gradient; annealing the amorphous solids formed at 90 K to the range 160–250 K, and using high pressure conditions, have been reported previously [1, 2]. A brief account of the high-pressure spectra of the present compounds has already been published [4], and shows the advantage of the Fourier-transform technique for high-pressure spectroscopy. Unfortunately, the BIC sample employed [4] w² contaminated with DBC and DIC and the present BIC high-pressure spectrum should therefore be preferred.

Raman spectra of the solids at low and ambient temperature were recorded with a 5145-Å argon ion laser of moderate power (ca. 300 mW). Solutions of BIC and DIC, however, were rapidly discoloured on excitation with the argon ion laser, but reasonably good spectra were obtained using a helium—neon laser if fresh solutions were supplied every 30 min.

RESULTS AND DISCUSSION

IR spectra of the solids annealed to ca. 205 and 250 K taken at 90 K are shown in Figs. 1 (DIC), 3 (BIC) and 6 (DBC). In order to restrict the number

of spectra published, the range shown is limited to 1500–980 cm⁻¹ in Figs. 1, 3 and 6, although equally interesting features were observed below 1000 cm⁻¹. Corresponding Raman curves for the two crystalline solids annealed at the same temperatures are shown in Figs. 2 and 7 for DIC and DBC, respectively.



Fig. 1. IR curves of *trans*-1,4-diiodocyclohexane (DIC) at 90 K; upper spectrum 1460–1220, lower 1220–980 cm⁻¹. Solid lines, sample annealed at 205 K (aa conformer); dashed lines, sample annealed at 250 K (ee conformer).



Fig. 2. Raman spectrum of *trans*-1,4-diiodocyclohexane (DIC) at 90 K; solid line, annealed at 205 K (predominantly aa conformer); dashed line, annealed at 250 K (ee conformer).



Fig. 3. IR curves of *trans*-1,4-bromoiodocyclohexane (BIC) at 90 K; upper spectrum 1460—1220, lower 1220—980 cm⁻¹. Dotted lines unannealed, amorphous solid; solid lines, sample annealed at 205 K (aa conformer); dashed lines, sample annealed at 250 K (ee conformer).



Fig. 4. The IR dichroism spectrum of an oriented polycrystalline film of *trans*-1,4-bromo-iodocyclohexane (BIC).



Fig. 5. The IR spectrum of *trans*-1,4-bromoiodocyclohexane (BIC) in a diamond anvil cell at ambient temperature; $1500-600 \text{ cm}^{-1}$ (Ge beamsplitter, 2-cm⁻¹ resolution, 200 scans), $600-200 \text{ cm}^{-1}$ (3.5 µm beamsplitter, 2-cm⁻¹ resolution, 200 scans), $200-75 \text{ cm}^{-1}$ (16-cm⁻¹ resolution, 300 scans). Solid line represents negligible pressure (ee conformer), dashed line ca. 50 kbar pressure (predominantly aa conformer).



Fig. 6. IR curves of *trans*-1,4-dibromocyclohexane (DBC) at 90 K; upper spectrum 1460—1220, lower 1220—980 cm⁻¹; for meanings of dotted, solid and dashed lines, see Fig. 3.



Fig. 7. Raman spectrum of *trans*-1,4-dibromocyclohexane (DBC) at 90 K; for meanings of solid and dashed lines, see Fig. 2.

The dichroism of a partly-oriented crystalline film of BIC is reproduced in Fig. 4. A high-pressure IR spectrum of BIC is given in Fig. 5, together with an analogous spectrum at ambient pressure. High-pressure spectra of BIC and DIC in the low-frequency region have already been published [4].

The observed IR and Raman bands of DIC are listed in Tables 1 and 2, respectively, while the IR and Raman bands of BIC are given in Table 3. Corresponding data for DBC were given in an earlier paper [1]. New results for DBC from the low-temperature spectra, crucial for the spectral assignments, and new high-pressure data in the region below 300 cm^{-1} have been listed in Table 4.

IR spectra of DIC as a melt and as a solid above 450 cm^{-1} , and incomplete Raman spectra of the solid have been published by Remizov and Sverdlov [5], combined with a force constant calculation for this molecule. BIC has not previously been synthesized to our knowledge.

DIC, like the other symmetric compounds DCC and DBC, will obviously have C_{2h} symmetry [5] for both conformers and mutual exclusion between the Raman (14 $a_g + 10 b_g$) and IR-active (11 $a_u + 13 b_u$) modes. This is easily verified from Tables 1 and 2. BIC will have C_s symmetry, like CBC and CIC [2], with all the fundamentals (27 a' + 21 a'') active in both spectra. However, pseudo C_{2h} symmetry is introduced by the similarities between the substituents, and so most of the strong IR bands in BIC are weak in the Raman and vice versa (Table 3).

Conformational equilibria

The conformational equilibria of DIC and BIC are similar in practically every respect to those of DCC, DBC, CBC and CIC. These features have been thoroughly discussed in previous papers [1, 2] and will be mentioned only briefly in this contribution.

Several IR and Raman bands present in the melts or solutions of DIC or BIC

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IR spectral data^a for trans-1,4-diiodocyclohexane

Solution	Crystalline			Interpreta	ation
CCl ₄	90 K (I) ^b	90 K (II) ^c	50 kbar	<u>ee</u>	
	*	2961 m ^d			comb.
2952 s	2950 s	2942 s		ν_{36}	ν ₃₆
	2942 s) 2937 w.sh			Vas	
2925 m sh	2929 m	2913 w		Van	V
2020 11,51	2913 m J	2010		comb	- 25
2896 m	2884 m	2893 s		comb.	ν ₃₇
2861 m	2860 w,sh 2854 w	2854 m		ν_{26}	ν_{38}
2840 w	2850 m	2829 s		ν_{38}	ν_{26}
	2045 W)		1489 w	comb.	
1450 s	1448 m 1446 s	1452 w,sh		V 39	comb.
1445 w,sh 1436 s	1440 s 1436 m	1443 s 1438 m	1447 s	<i>v</i> ₂₇	ν ₃₉
	1428 w	1434 m 1429 m		comb.	comb.
1429 m	*	1423 s 1420 s	1431 s		V 27
1426 w,sh		1411 m			comb.
1402 vw	1402 vw 1395 vw }	1400 vw	1404 w	comb.	comb.
		1360 s)	1377 W	V 28	
1359 m	1352 w,I_{\perp}	1354 s	1358 s	comb.	v ₂₈ , v ₄₀
	$1341 \text{ m} \\ 1335 \text{ w} $ I_{\perp}	1341 vw 1335 vvw	1343 m	v 40	
	1325 w,I_{\perp}	1326 vw	1331 m	comb.	
1304 w	1313 vw 1301 vw	1302 s	1304 m	comp.	ν_{20}
1284 ww	1285 s } I		1289 m	V	17
1201 10	1282 w,sh) ~" 1266 w.sh	1263 w.sh	2000	comb.	comb.
1263 m	1259 vs 1253 wsh I_{\perp}	1259 m	1262 m	v_{41}	
	1244 vw	1248 vw	1246 w	comb.	comb.
1231 vs	1226 vw	1225 vs	1230 vs		ν_{41}
	1213 vw 1210 vw	1215 w,sh		comb.	comb.
1204 w	1201 s,I	1201 w	1208 s	ν ₃₀	
1172 VVW	* *	1158 vw) 1153 vw)	1173 W	comb.	v 30, v 42

TABLE 1 (continued)

Solution	Crystalline			Interpreta	ation
CCl₄	90 K (I) ^b	90 K (II) ^c	50 kbar	ee	<u>aa</u>
	1139 w }			comb.	
1190 -	1135 w,sh J *	1132 s	1135 m.sh		ν.,
11295	1124 s)	1124 m	1199 c		31
1119 m,sn	1121 s	1121 m /	11225	V 42	
1110 w	1113 w	1117 w,sh 1113 w		comb.	comb.
1095 vw	1106 w 1100 vw	1110 vw		comb.	
	1084 vw,I		1092 w	comb.	
	1079 w 1074 w		1080 w	ν ₃₁	
	$1037 \text{ vw} \\ 1032 \text{ vw} \mathbf{I}_{\parallel}$	1032 vw	1034 w	comb.	comb.
1025 vw ^e	1018 m,I ₁	1018 vw	1020 m	comb.	
	*	1013 vw }			comb.
	005 mm)	1005 S) 1002 S)			
1000 s	990 vw	998 vs	1003 s	comb.	ν_{43}
985 s	985 vs,I ₁	986 m	985 m,sh	ν_{43}	
	978 w)				
	972 W) 966 w sh	966 w			comb.
	0.47	949 w)	052		
943 vw°	947 W	941 w)	900 W	² 32	V 32
	923 w *	907 m ab	926 w	comb.	comh
893 w	891 s.I.	891 w	895 m	<i>v</i> , ,	comb.
000	*	885 w,sh		33	comb.
883 m	880 s,I ₁	880 w	880 m	ν_{44}	
	877 w			comb.	
0.04		866 vs)	969 6		*1 *7
864 m	864 vw	860 m)	000 \$		V 33, V 34
	854 vw		0.07	comb.	
	829 vw	804 100	810 yw	comb.	
	760 vw)	760 w)	510 VW	comb.	a a mah
740 vw ^e	750 vw)	749 w)	752 vw	comp.	comb.
707 s	707 w,sh	$\sim 701 \text{ vs}$	708 s	Vas	V ₁₅
703 s)	700 vs, I_{\perp})	101 13	703 w,sh)		43
	693 w 680 mm			comb.	
	635 vw)			comb.	
	631 vw)		644 vw	comb.	
618 vw ^e	604 vw	605 vw	607 w		comb.
			570 w		comp.
460 m	*	460 s,sh	468 s		v 46

TABLE 1	(continu	ed)
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Solution	Crystalline		Interpretation			
CCl ₄	90 K (I) ^b	90 K (II) ^c	50 kbar	ee	aa	
412 m ^f	407 m,I	407 vw	409 m	VAG		
346 vw? ^f	*	357 vw	354 vw	-0	comb.	
295 s ^f	296 s,I⊥	296 m	313 w 295 s	V 47	ν_{34}	
270 m ^f	278 w,sh ^g	271 s	274 m		VAT	
235 w ^f	231 w ^g 165 vw ^g		235 m	V 34		
129 w ^f	133 w ^g		138 s	ν		
114 w ^f	*		110 w	33	V 35	
$\left. \begin{array}{c} 84 \ w^{h} \\ 73 \ w^{h} \end{array} \right\}$	84 m ^g		93 s	ν_{48}	V _{AB}	

^aWeak bands outside the fundamental regions 4000–3000 and 2700–1500 cm⁻¹ are omitted. ^bCondensed from vapour at 90 K, annealed at 250 K and recooled to 90 K. ^cCondensed from vapour at 90 K, annealed at 205 K and recooled to 90 K. ^ds, strong; m, medium; w, weak; v, very; sh, shoulder; bd, broad; I_{||} and I₁, dichroic measurements; asterisks (*), bands which are absent; comb., combination band. ^eBands observed in CS₂ solution. ^fBands observed in C₆H₆ solution. ^gPolyethylene pellets at room temperature. ^hBands observed in cyclohexane solution.

vanished in the solid-state spectra. Comparison with the other cyclohexane spectra [1, 2] reveals beyond doubt that the solid-state bands belong to the ee and the vanishing bands to the aa conformers.

A systematic study of the band intensities of DIC and BIC in various solvents was not carried out. However, it was apparent from e.g. the band pairs 1000 (aa) and 985 cm⁻¹ (ee, v_{43}) in DIC and 716 (aa) and 724 cm⁻¹ (ee, v_{20}) in BIC that the ee band is enhanced relative to the aa band in the solvents CCl₄, CS₂ and C₆H₆. Thus the equilibrium was displaced towards the ee conformer for DIC and BIC in the more polar solvents, as reported in detail for DCC and DBC [1, 6, 7]. This may be interpreted as a result of the higher quadrupole moment of the ee conformer [7].

It has been reported [5] that as bands appeared in the IR spectra of DIC crystals upon heating before the melting point was reached. We did not repeat these experiments for DIC or BIC, but the results [5] are in complete agreement with data first reported for DCC by Yoshino [8] and discussed in considerable detail by us for DCC, DBC [1], CBC and CIC [2].

Various mono- and dihalogenated cyclohexanes with chloro- and bromosubstituents crystallize in thiourea clathrates in the a (aa) conformation only, while for iodocyclohexane additional amounts of the e conformer were also present [9, 10]. It is significant that DIC, BIC, and CIC, all of which contain the large iodine substituent, are accommodated as mixtures of (predominantly) aa and ee conformers in the thiourea clathrates. DCC, DBC and CBC [2, 10], on the other hand, can apparently be packed more efficiently in the thiourea channels as aa conformers and practically no ee bands were detected.

Raman spectral data^a for trans-1,4-diiodocyclohexane

Solution	Amorphous	Crystalline		Interpret	tation
C₅H₅	90 K	90 K (I) ^b	90 K (II) ^c	ee	aa
	2964 m ^d	*			comb.
	2946 s	2951 s		ν,	ν,
		2943 m J		· .	i.
		2934 w		comb.	
	2915 m	2920 w,sn (ν_{15}	ν_2
	2898 w	2914 m)		12	
	2000 •	2886 w 1		,	
	2884 w	2877 w		comb.	ν_{15}
	0050	2859 w.sh			
	2853 m	2851 m		ν_{3}, ν_{16}	
	2827 w	*			v_{3}, v_{16}
	1452 w	1454 w		ν,,	-
1436 w	1437 w	1437 w	~1430 w,bd	ν_{4}	ν_{i7}
1404 w,P	1430 w,sh		1423 vw		$\nu_{_4}$
	1345 w	1349 m,sh	1348 vw	ν_{18}	ν_5, ν_{1R}
1328 m,P	1328 m	1329 s	1325 vw	ν _s	
1310 w,sh	1300 vw	1307 w 1293 w	1 297 vvw	V 19	<i>v</i> ₁₉
1269 w	1272 w	*	3270 w		ν_6
1251 s,P	1247 s	1249 s	1247 w	ν ₆	
1182 m,P ^e	1184 s	1187 s	1183 w,sh	υ,	
1166 m,P ^e	1170 m	*	1169 m		ν_{7}, ν_{20}
	1143 w	1145 w		V 20	
	1123 w	1125 w	1122 vw	comb.	
1058 m	1054 m	1057 s	1055 vw	ν_{8}, ν_{21}	ν_{21}
1023 m	1029 s	*	1025 m		ν_{8} .
	1012 vw	*	1010 vw		comb.
990 m ^e	992 s	997 vs 990 w,sh	992 w	v,	ν,
	816 m	816 s,sh)	807 m		13 11
	809 w,sh J	812 s 🕽	007 m	² 10	U 107 U 22
		787 w		ν_{22}	
201 D	405	649 w		comb.	
631 s,P	625 vs	628 vs	625 s	ν ₁₁	
587 w,sh	590 w,sh	593 m	590 w,sh	comb.	
581 m,P	584 m		580 s		ν_{11}
400 S,r 427 w P	400 s 426 w	400 VW	460 S	ν ₂₃	ν_{12}, ν_{23}
321 c P	420 W 334 c	421 W	222 c	V 12	
001 5,1	247 July 5	949 w	000 8	.,	V ₁₃
226 s	228 w	232 w	229 w?	V 24	9
128 s P	131 \$	135 vs	130 w	² 13	~ 24
93 m	95 w	*	97 w	-14	<i>v</i>
	••				14

^aThere are no data available for solution or the crystalline state (II) at frequencies higher than 1500 cm⁻¹. ^bCondensed from vapour at 90 K, annealed at 250 K and recooled to 90 K. ^cCondensed from vapour at 90 K, annealed at 205 K and recooled to 90 K. ^dFor abbreviations, see Table 1; P, polarized. ^eBands observed in CCl₄ solution.

Low-temperature crystals

We have discussed in considerable detail our annealing experiments with DCC [1], CBC and CIC [2]. Firstly, an amorphous glass, containing both the ee and the aa conformers, was formed at 90 K by shock-freezing the vapour on a CsI window (IR) or copper plate (Raman). When carefully annealed to higher temperatures, each of the six compounds in this series first formed solid phases ("aa crystal") consisting of molecules in the aa conformation, while at higher temperatures the common "ee crystal" was present. The amount of ee conformer appearing in the "aa crystal" and the optimal annealing range varied somewhat between the compounds. IR curves for DIC, BIC and DBC are shown in Figs. 1, 3 and 6, respectively, while Raman curves for DIC and DBC are given in Figs. 2 and 7.

The dotted lines in Figs. 3 and 6 represent the IR spectra of the amorphous phase, which were not included in the Raman (Figs. 2 and 7) or in Fig. 1. In all the figures the solid lines represent the spectra of a solid phase annealed to ca. 205 K (ca. 10° higher than the corresponding experiments for CBC and CIC [2]) and subsequently recooled to 90 K. In the most successful recordings the amount of aa conformer in this phase was ca. 96% for DIC, 94% for BIC and 88% for DBC, estimated from band intensities of the solid curve at ee band maxima. In spite of repeated annealing experiments at different temperatures for extended periods of time (0.2–2 h), we were not able to remove the remaining ee bands from the spectra.

On heating the compounds to temperatures in the region 230-270 K for 0.5 h and recooling them to 90 K, the spectra contained only bands characteristic of the ee conformer (dashed lines in Figs. 1-3, 6 and 7). After the "ee crystal" had been formed, no subsequent annealing in the 160-210 K temperature range would restore the aa conformer, and we therefore believe the aa-containing solid to be a metastable crystalline phase. Though all the IR and Raman spectra in Figs. 1-3, 6 and 7 were recorded at 90 K, the aa and ee curves are quite similar to those recorded at the annealing temperature (ca. 205 and 250 K, respectively).

Frequent cases of factor-group splitting were observed for the crystals of the stable ee conformer of the symmetric compounds DCC [1], DBC and DIC. It is highly significant that a similar splitting was also found for the apparently metastable aa-phases, e.g. 466, 460 and 1434, 1429 cm⁻¹ for DIC and 1365, 1360; 1368, 1366; 1244, 1238 and 876, 871 cm⁻¹ for DBC. Thus, it seems highly probable that the solid phase containing the aa conformer is crystalline. We assume that this conclusion is also valid for the asymmetric compounds CBC, CIC and BIC, but the appearance of factor-group splitting is more uncertain in these cases.

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IR				Raman			Interpretation	U
Melt	Crystalline			Solution	Crystalline		ee	аа
400 K	90 K (I) ^b	90 K (II) ^c	50 kbar	ccı	90 K (I)	90 K (II)		
2972 w,sh ^d	*	2968 w,sh	2972 m		*	2966 s		comb.
2955 s,sh	2955 s }	2955 m	2947 s		2952 s	2948 s	P 1, P 2	V 11 V 2
1 5 6 7 6 7	2935 m	1 0 7 6 7			2939 w.sh		<i>ود لا</i>	
2921 w	2921 m 2913 w.sh	2921 w	2928 w		2917 m		ν ₃ , ν ₂₉ comb.	V 28
2901 m	*	2901 m	2900 s		2904 w		V4	ν, υ ₄
	2891 w 2883 vw.sh	2887 m			2890 w,sh 2877 w.sh	2888 s	comb. comb.	V 29
2859 m	2856 m) 2852 m)	2857 m	2858 m		2853 w	2860 m	ν ₅ , ν ₆ , γ	٣s
2838 w	*	2833 m	2834 m			2832 m		V ₆ , V ₃₀ , V ₃₁
		1463 vw						comb.
	1452 m	1454 m		1460 vw	14 ⁻ 5 w		₂₆ س	
1450 s	1449 s	1450 m					<i>4</i> م	
	1444 m	1444 vw,sh					comb.	
1438 w,sh	1439 vw	1440 m		1439 w	1436 m	1440 w	ν ₈	V 32
1435 s	1433 w,sh,I	1436 m }	1448 s				¢¢ ۷	۳,
1427 s	*	1426 s	1424 vs,bd	1427 w	*	1425 w		U _{R1} U ₃₃
		1420 w,sh						comb.
	1379 w ^e						P ₃₄	
1359 m	*	1363 m 1357 s	1367 s					ν ₉ , ν ₃₄ , DIC
	1350 vw	1350 w,sh	1358 s	1350 vw	1351 w	1352 w	₃₅ ل	V 101 V 35
1346 m	1344 m,sh 1342 s.I.	1342 w	1344 m				comb. ″。	
	+ -						•	

IR and Raman spectral data^a for trans-1,4-bromoiodocyclohexane

TABLE 3

		V ₃₆	₇₆ ۷		۳ ₁₁			DBC	<i>ل</i> ارو	DIC			V ₁₃	comb.	И ₃₈	0[Λ t ₄₁ V	. חות						ν_{41}	V 15	comb.	ν ₁₆ , ν ₁₇ , DBC
comb. comb.	ν10, DIC	comb.		V361 V37		ν11, DBC	<i>v</i> ₁₂ , DIC				comb.	V13, V38	DIC		DBC	V 141 V 39			comb., DIC		V ₄₀	COILID.	v15, v41, DIC		comb.	^ν ι, DIC
	1329 w	1304 w			127 3 m	1257 w	1249 w,sh					1200 w,sh	1187 m		1161 m			m c211					1063 vw	1029 m		998 m
	1329 s	1310 w		1294 w	*		1249 s					1199 s	11 85 w		*	1143 m			1123 w				1067 m.) 1057 w)	*		998 s
	1332 m,P	1310 vv			1274 m		1252 s, P					1199 m,P	1186 m,P		1163 vw	1146 w		1129 w					1063 w,bd	1029 m		996 s,P
		1311 m	1307 m,sh	1289 m		1266 s			~ 1250 vs,bd	~1227 s,bd		1209 w	1189 m			~1145 vs,bd		1128 s			1089 w		1072 m		1021 m	1006 vs,bd
		1308 w	1302 w	1289 w	1275 vw	1268 w) 1264 w)		1245 m	~ 1236 vs	1228 m,sh 1224 m,sh	1207 vw	1201 w	1187 m	1182 w	1165 w }	1151 m 1144 m	1138 w)	1133 m	1124 w) 1121 w)		1079 vw	1075 vw	1066 vw	1030 vw	1022 w } 1017 w }	1003 s 998 s
1339 m,sh	1329 vw	*	*	1289 m,I _{II}	1275 vw	1263 s,I ₁ \ 1260 m	1248 vw	*	*	*	*	$1201 \mathrm{ s,} \mathrm{I_{ }}$			$1162 \text{ m} I_{1}$ 1159 m I_{1}	1143 vs,I _L }	2 00TT		1124 s,I $_{ m L}$	1110 vw	1079 m,I	1075 w	1066 m, I_{1}		1021 m,I_{1}	$997 \text{ w,I}_{\mathrm{L}}$
		1308 w	1303 w	1285 w		1266 m		1246 m,sh	1238 s	1228 m		1202 m	1185 w		1166 vw	1146 s		1129 m			1075 w,sh		1066 w		1019 vw	8999 s

TABLE 3 ((continued)							
IR				Raman			Interpretation	
Melt	Crystalline			Solution	Crystalline		ee	aa
400 K	90 K (I) ^b	90 K (II) ^c	50 kbar	ccl4	90 K (I)	90 K (II)		
987 s	989 vs,I ₁	989 s	988 s,sh				ν'', DBC, DIC	
	976 w,I ₁						comb.	
	951 w,I	949 vw	959 w				V 42	
946 vw		942 vw	945 m					V 42
	929 vw *	929 vw 901 w					comb.	comb. comb.
895 m	895 s,I	894 w	497 s,sh				_{د ب} ۷	
885 s		888 w } 884 w }	888 s				ν, DBC	
865 s	878 w,sh	873s 868s	880 vs,bd			865 vw	DIC	ν ₁₈ , DBC, DIC
	*	861 m						И ₄₃
818 vw	817 w,I _L		828 w	820 m,P	818 s	823 w,sh 809 m	V 19	V19, V44
					790 w		P 44	
736 w	$732 \mathrm{~s,I_{1}}$	735 w	734 s,sh				DBC	
724 s	$720 \text{ vs,I}_{ m L}$	723 s	723 s		720 vw		لا ₁₀	DBC
716 s	709 w	713 vs	714 s					V 20
706 w 701 w	702 s,I ₁	701 m	707 s				DIC	DIC
	663 vw		672 w		662 w		comb., DBC	
	648 w,I _l		646 vw	653 s,P	650 vs	650 m	V 21	
	636 vw			636 m,P	634 s	635 m	comb., DIC	טמע
	*	592 vw	599 w	593 s.P	594 w	592 s	comb.	
			567 w 552 w					comb. comb.
			:					

v11, DBC	ν,,, DIC	ν ₂₃ , DIC			V 24				v DBC))) () f	v 25	DIC	<i>د</i> . ۲	47					V 45	V 26		
	V 45		ν ₂₂ , DBC	V 23	comb., DBC		V 24	comb.	DIC					9*	wv DBC		" " DBC	7261 7483 710	DIC		V27	
488 m	463 s		425 w	416 vw,sh	345 s						284 w		263 w	- 004			151 w	I TOT	131 vw			
*	460 vw				*		320 vw				*		265 w)	256 w J	235 w		151 m	III TOT	133 w		94 ww	
488 m	465 m ^f				345 m						286 m				937 m ^f		140 ° D	16 0 11	128 w	105 m,P		
493 s	472 w,sh	470 s	438 vw,sh	421 m	347 m		329 s	320 vw,sh	310 w ch	TRE MOTO	295 s	280 w _s h	963 ww		9.37 w		156 m)	145 m J	132 w	120 m	109 w,sh	
488 s	465 w,sh	460 m			341 w	325 vw	321 m		301 w	M TOO	285 m	271 w										
*		*	425 w	418 m,I_{1}	340 m		321 s	318 w,sh	708 11	A 0.27	*	*	060 wh	A 007	033 mh		155 w ⁿ)	145 w ^h)			89 w ^h	
488 m		459 m	429 w	419 w	340 w		$322 s^{g}$		302 s ^g \	296 w,sh ^g	285 s ^g	270 w ^g	260 w ^g	253 vw ^g	234 w,sh ^g)	227 w ^g	1 K		126 w ^g		93 w ^g	

in C_sH_s solution containing considerable amounts of DBC. ^hPolyethylene pellets at room temperature containing considerable amounts of DBC. amounts of trans-1,4-dibromocyclohexane (DBC) and trans-1,4-diiodocyclohexane (DIC). ^bCondensed from vapour at 90 K, annealed Table 1. ^eObserved in the high pressure cell after the pressure had been released. ^fBands observed in CHCl₃ solution. ^gBands observed at 250 K and recooled to 90 K. ^cCondensed from vapour at 90 K, annealed at 205 K and recooled to 90 K. ^dFor abbreviations, see ^aWeak bands outside the fundamental regions 4000-3000 and 2700-1500 cm⁻¹ are omitted. All the samples used contain small

IR and Raman spectral data^a for crystalline trans-1,4-dibromocyclohexane

IR		Raman		Interpretati	on
90 K (I) ^b	90 K (II) ^c	90 K (I) ^b	90 K (II) ^c	ee	aa
		*d	3000 m		comb.
*	2976 m	*	2975 s		comb.
2963 s)	2964 m j	2963 s		υυ	ν.,
2955 s	2957 w l	2957 s	9050 -	- 17 - 36	06
	2040 m)	2950 m	2900 \$		<i>v</i> ₁
2944 m	2945 m.sh			ν_{25}	comb.
2928 m)	0000	0007 -			
2922 w,sh	2929 W	2927 s		U15, U37	V 25
		2919 m,sh		ν,	
44	0000	2913 m,sh J		÷	
*	2908 m	*	2904 c		ν_{37}
2903 w sh)			2504 5		2, 1,5
2896 w		2899 m		comb.	
*	2889 w	2884 w		comb.	?
2865 m	2865 w	2869 w	2863 m	V 37 V 16	U 37 U 16
2862 m	2858 11	2860 s)		ν_{26}, ν_{38}	
2007 m /	2843 vw sh)				- 3×
*	2838 m				ν_{26}
*	2832 w)				comb.
	2830 w J				,
		*	2827 W		comb.
1456 m	1456 w	1460 m	1460 W,Sh	comb	
1452 s	1450 w			ν,,,	
1447 m)	1445 m)				b
1443 m 🕽	1443 m			comb.	comp.
1439 vw)	1439 m }	1440 m	1437 m	V V	V V
1435 w)	1437 m J	1110	1101	- 49 - 27	- 171 - 39
*	1433 m				
*	1431 m 1498 w ch	*	1497 m		ν ₂₇ ν.
*	1420 w,sh^{2}		1121		4
*	1422 w,sh				comb.
*	1419 w,sh				
*	1368 m				ν_{78}
	1366 m J				25
*	1365 W,Sn				ν_{40}
	1357 m \	1050	1050		
*	1353 w	1356 w	1356 w	ν_{1*}	v_{5}, v_{18}
1348 w				comb.	
1344 s	1344 w }			V.o	
1342 s 🕽	1342 w J			~ 40	

TABLE 4 (continued)

IR		Raman		Interpretatio	n
90 К (I) ^ъ	90 K (II) ^c	90 K (I) ^b	90 K (II) ^c	ee	aa
1338 vw,sh		1335 s	1333 w	ν ₅ , comb.	
*	1312 w 1309 w	1315 w	1307 w	comb.	v ₁₉ , v ₂₉
1297 w 1292 m	1292 w	1295 m		<i>v</i> ₁₉ , comb.	
1290 m 1286 vw	1290 w	*	1279 s	ν ₂₉	ν ₆
1274 w	1274 w 1271 w			comb.	comb,
1267 s 1266 s	1266 m 1265 w,sh			ν_{41}	
	1255 vw	1254 s	1255 w,sh	ν ₆	comb.
*	1244 vs 1238 s	1240 vw		comb.	<i>v</i> 41
*	1230 vw 1224 w				comb.
		1211 s		ν,	
1203 m	1202 w	*	1205 s	<i>v</i> ₃₀	ν,
1200 w,sh				comb.	
1178 vw,sh 1175 w	1172 w			comb.	comb.
1168 s 1165 s	1168 w,sh 1166 m)	*	1166 m	v ₄₂	ν ₂₀
1162 s,sh 1160 s	1162 m J 1160 m			comb.	- 30
		1152 m		ν_{20}	
*	1150 vw 1145 vw				comb.
1141 vw				comb.	
*	1136 w 1129 vw				ν ₃₁
1126 vw *	1199	1125 w	1127 m	comb.	comb.
	1122 W	1082 m	1085 w	ν_8	comp.
1081 m 1077 vw	1081 w			ν_{31}	
		1062 w	1062 vw	ν_{21}	ν_{21}
1030 w 1026 w	1027 vw	*	1030 s	comb.	$\nu_{_{R}}$
1002 s	1006 s 1001 s	1005 vs	1005 m	ν ₉ , comb.	ν_{9}, ν_{43}
*	997 w,sh				comb.
990 vs	991 s			V 4 3	
983 w	988 w,sh			comb.	
ษ <i>า</i> 2 พ 955 พ	972 W 953 vw			comb.	comb.

IR		Raman		Interpretati	on
90 K (I) ^b	90 K (II) ^c	90 K (I) ^b	90 К (П) ^с	ee	aa
*	945 w				ν ₃₂
930 w	930 vw			comb.	_
919 vw	920 vw			comb.	comb.
*	904 vw				comb.
899 m }	897 w			V	
897 m,sh J				33	<u> </u>
*	892 w				?
887 s	887 m			VAA	
886s)					
883 w,sh				comb.	
881 w /	$(\mathbf{r}, \mathbf{r}, \mathbf{r})$				
*	8765				ν_{44}
	871 s J				
0.01	863 m				33
861 W	959				
	841 yw				comb.
	041 VW)	823 s		ν.	
		*	812 s	- 10	V V
		792 vw		ν	103 * 22
		*	770 vw	- 11	comb.
766 w.sh)				h	o a male
759 m	760 m,ba			como.	comb.
600	735 s			-	aamb
133 VS	733 m			V 45	comb.
727 m)	795 vc)			comb	
722 w 🕽	723 s ch			como.	ν_{45}
	723 S,SI 7				
*	714 yrsz				?
706 w	114 (117)			9	
100 1		685 m	688 w	comb.	
		663 vs	667 s	ν	
		*	604 vs	- 11	ν.,
553 vw				comb.	
503 vw	497 s)				
*	491 s				D 46
		*	485 vs		ν_{12}
*	484 w,sh				comb.
		455 w		V 23	
446 vw	440 vw			?	comb.
434 w	434 vw			?	
		430 m	433 vw	ν_{12}	
429 m	429 w			ν	
427 m,sh)				40	
383 vw		÷	054	comb.	
941 -	241	*	304 VS		ν_{13}
041 S 299 me	341 M 322 mf				31
044 III	024 111			comp.	~ 34

TABLE 4 (continued)

TABLE 4 (continued)

IR	,	Raman		Interpretati	on
90 K (I) ^b	90 K (II) ^c	90 K (I) ^b	90 K (II) ^c	ee	aa
*	307 s ^f				ν47
			288 vw?		ν_{24}
	_	266 m	265 vw	V 24	
235 m ^e	238 m ^r	243 s	238 vw	ν_{13}, ν_{34}	?
		174 vs	174 vw	ν_{14}	
158 s ^e	164 s ^f			ν ₁₁	?
	145 m ^f				ν.,
134 vw ^e					
95 s ^e	100 s ^f			U 48	

^aWeak bands outside the fundamental regions 4000—3000 and 2700—1500 cm⁻¹ are omitted. More complete spectral data are given in ref. 1. ^bCondensed from vapour at 90 K, annealed at 250 K and recooled to 90 K. ^cCondensed from vapour at 90 K, annealed at ca. 205 K and recooled to 90 K. ^dFor abbreviations, see Table 1. ^eBands observed at room temperature with the high pressure cell after the pressure had been released. ^f50 kbar nominal pressure [11].

High-pressure studies

When the solid samples of DIC, BIC or DBC were compressed to 10-50 kbar nominal [11] pressure in a diamond anvil cell, as bands appeared while the ee bands diminished in intensity. The three compounds behaved quite similarly under pressure, and so only the spectrum of BIC is shown (Fig. 5). The curves (dashed line, 50 kbar nominal [11] pressure; solid line, negligible pressure) were obtained from interferograms using three different beam-splitters, the same sample being used for all spectral regions.

The curves show clearly that the bands are frequently shifted to higher wavenumbers under pressure and the solid is converted to a phase containing largely the aa conformer. In BIC there is still ca. 15% of the ee conformer present at 50 kbar nominal [11] pressure, in DBC ca. 15% and in DIC ca. 25%. Of the six compounds studied, only DCC [1] was completely converted to the aa conformer under pressure.

As discussed previously [1, 2], the gradual conversion of the ee to the aa conformer with pressure suggests either that the two conformer molecules exist in the same crystal lattice or that the ee phase is converted to an aa phase through a higher-order phase transition. More high pressure work under carefully controlled conditions is needed to resolve these problems.

Quantitative studies in CS_2 solution gave the following increases in the equilibrium constant K = [axial]/[equatorial] per kbar [12]: 11.5 ± 0.6 (DCC) and 15.4 ± 0.6 (DBC), compared to 7.3 ± 0.4 for chlorocyclohexane. The difference in partial molar volumes should be 2.8 and 3.8 cm³ mol⁻¹ for DCC and DBC, respectively. Thus, at a defined pressure, e.g. 10 kbar, the conformational equilibrium in CS_2 solution is displaced further towards aa

for DBC than for DCC. In the crystalline state, however, DCC is more completely converted to the aa conformer with pressure than any of the other five *trans*-1,4-dihalocyclohexanes. Various molecular and crystal parameters determine the nature of the conformer, though the ee—aa conversion in the solid state is not very well understood [2].

Spectral interpretations

The observed IR and Raman bands which are assigned as fundamentals for the ee and aa conformers in Tables 1–4 are listed in Table 5 (DIC and DBC) and Table 6 (BIC). The fundamental frequencies are compared with the results of our extensive force constant calculations, which will be described in detail in a forthcoming paper [13]. A 49-parameter force field which was common to practically all the 12 conformers of the six *trans*-1,4-dihalocyclohexanes was derived. In the final computations iteration was carried out to provide the best possible fit between about 600 observed and calculated frequencies.

The assignments are based upon the large bulk of experimental data available for the *trans*-1,4-dihalocyclohexanes. Since we have been able to isolate both the ee and the aa conformers in each of the six compounds (by annealing the amorphous phase and by high-pressure techniques), we have considerable confidence in our interpretation. We believe that the set of fundamental frequencies assigned for each conformer of the series [1, 2] is more reliable than anything achieved for any molecule of comparable size undergoing conformational equilibria. Nevertheless, there are still a number of uncertainties in the spectral interpretations which may be subject to further improvements. This is illustrated by Table 5, where the numbers in italics represent the DBC fundamentals revised relative to the original assignments [1] on the basis of our new data including: (1) the metastable aa crystal and (2) the results from the force constant calculations.

Obviously, the spectra of the symmetric compounds DCC, DBC and DIC which display mutual exclusion between IR and Raman bands can be interpreted more easily than those of CBC, CIC and BIC. In the last three molecules, all the 48 fundamentals for each conformer are active in both IR and Raman, and consequently these spectra appear crowded. Vibrational bands associated with the ee and aa conformers frequently overlap in these molecules and there are various coincidence possibilities: fundamentals (ee) fundamentals (aa); fundamentals (ee)—comb. bands (aa); fundamentals (aa)—comb. bands (ee) and comb. bands (ee)—comb. bands (aa). Fundamentals and combination bands of the same conformer with the same or with different symmetry species can also overlap.

The spectral assignments for DIC are given in Tables 1, 2 and 5, while those for BIC are listed in Tables 3 and 6. Although the spectra of DBC have been discussed in a previous paper [1], the new results (particularly the IR and Raman annealing experiments, which provided spectra of the pure as conformer) made it necessary to revise the assignments. The new experimental data

	trans-1,4-Diiodocyclohexane				trans-1,4-Dibromocyclohexane				
	ee		aa		ee		aa		
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
ag									
ν_1	2950	2955	2950	2955	2962	2956	2962°	2956	
ν_2	2900	2919	2915	2919	2914	2919	<i>290</i> 8	2919	
ν	2855	2856	2833	2855	2866	2856	2843	2855	
V ₄	1436	1436	1430	1425	1442	1437	1427	1425	
ν ₅	1328	1332	1350	1341	1337	1334	1354	1343	
ν	1251	1244	1269	1264	1258	1247	1278	1272	
ν_7	1182	1182	1166	1175	1212	1211	1204	1212	
ν_8	1058	1064	1023	1039	1084	1081	1034	1046	
v,	990	996	990	1000	1004	1001	1004	1011	
v_{10}	812	811	816	806	826	823	810	814	
ν,,	631	639	581	578	674	678	611	605	
ν_{12}	427	426	460	455	434	431	489	489	
ν _{ι 3}	226	226	331	331	238	244	355	361	
ν_{14}	128	128	93	76	178	172	122	102	
b _g	0015	0012	0005	0010	0000	0010	0007	0012	
ν_{15}	2915	2913	2889	2913	2926	2913	2907	2913	
V16	2855	2852	2833	2851	2866	2852	2843	2851	
ν_{17}	1400	1957	1430	1440	1404	1447	1442	1950	
V ₁₈	1310	1337	1300	1330	1307	1301	1307	1300	
V 19	1310	1310	1305	1314	1150	1317	1317	1320	
<i>v</i> ₂₀	1140	1004	1055	1057	1152	1140	1069	1000	
V 2 1	799	1064	1055	706	1062	1065	1002 810	2062	
22	450	194	100	190	194	190	470	400	
ν_{23}	400	404	460	408	400	400	470	460	
D 24	241	202	220	241	200	201	202	212	
a_{u}	2937	2918	2920	2917	2939	2918	2923	2917	
V	2861	2855	2830	2854	2860	2855	2841	2854	
. 0 V	1436	1439	1429	1434	1438	1442	1427	1435	
ν	1377	1381	1359	1356	_	1384	1364	1358	
V	1284	1273	1304	1318	1288	1274	1312	1323	
ν ₂₉	1204	1204	1155	1151	1203	1205	1166	1161	
ν	1070	1072	1129	1128	1080	1081	1132	1132	
י א עיי	947	957	943	952	961	963	947	956	
ν	893	897	860	859	896	899	861	861	
ν	235	232	295	307	235	236	329	333	
ν_{35}^{-34}	129	118	114	95	155	143	129	113	
bu									
V 36	2952	2955	2952	2956	2960	2956	2960	2956	
ν ₃₇	2925	2916	2896	2916	2923	2916	2909	2916	
V 38	2840	2852	2861	2852	2860	2852	2860	2852	
V 39	1450	1451	1436	1451	1453	1452	1438	1452	

Observed^a and calculated^b fundamental frequencies for *trans*-1,4-diiodo- and *trans*-1,4-dibromocyclohexane

.

	trans-1,4-Diiodocyclohexane				trans-1,4-Dibromocyclohexane				
	ee		aa	aa		ee		aa	
_	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
b,,							· ··· ··		
- ~40	1340	1351	1359	1349	1348	1354	1360	1351	
ν_{41}	1263	1243	1231	1222	1267	1248	1245	1236	
ναη	1119	1119	1155	1150	1166	1159	_	1186	
ν_{43}	985	982	1000	996	988	990	1003	1004	
VAA	883	875	864	860	886	882	869	867	
ν_{45}	703	714	707	691	738	743	728	717	
V 46	412	420	460	454	430	436	495	498	
V 47	295	296	270	272	342	341	303	306	
V 48	84	61	73	65	96	73	—	81	

TABLE 5 (continued)

^aWhen possible, frequencies are taken from solution spectra. ^bA 49-parameter force field was derived and the calculated frequencies fitted to ca. 600 observed fundamentals of the ee (e) and aa (a) conformers of six *trans*-1,4-dihalocyclohexanes and monocyclohexanes; details are given in ref. 13. ^cFrequencies in italics are revised relative to those in ref. 1.

for DBC are given in Table 4, while the assignments are listed in Table 5, with the revised fundamentals printed in italics.

It is immediately apparent from Tables 5 and 6, particularly when compared to Table 3 of ref. 2, that the six *trans*-1,4-dihalocyclohexanes have strikingly similar spectra. The normal vibrations of the three asymmetric molecules CBC, CIC and BIC are described on the basis of C_{2h} symmetry and are combined with those of DCC, DBC and DIC in ref. 13. Both ee and aa fundamentals reveal a nearly monotonic relationship when listed in the order DCC, CBC, DBC, CIC, BIC and DIC [13].

The position of the vibrational modes in the asymmetric molecules can be correlated in a somewhat naive way with the corresponding modes in the appropriate symmetric molecules. Thus, the arithmetic mean of the *i*th normal vibration of DCC and DIC, $\frac{1}{2}[\nu_i(DCC) + \nu_i(DIC)]$, agrees very well with the *i*th fundamental frequency of CIC. A table demonstrating this relationship for the ee conformer is presented elsewhere [14]. Five similar tables correlating the ee as well as the aa conformer bands of CBC, CIC and BIC were constructed from the DCC—DBC, DCC—DIC and the DBC—DIC bands, respectively. In each case the correspondence was remarkably good. The deviations provided by $\nu_{11}(a_g)$ and $\nu_{45}(b_u)$ in the ee conformation of DCC and DIC [14] demonstrate strong interaction in the a' species of CIC, causing one band to be pushed up and one down in frequency.

The spectral region around 1000 cm^{-1} has been successfully employed to study the conformational equilibria in halocyclohexanes [15], pseudohalocyclohexanes [16] and *trans*-1,2-dihalocyclohexanes [17]. Well-separated, pure e or a bands which are intense both in IR and Raman are situated around 1000 cm^{-1} , the axial conformer invariably giving rise to the higher-frequency

	ee		aa			ee		aa	
	Obs.	Calc.	Obs.	Calc.		Obs.	Calc.	Obs.	Calc.
<u>a</u> '									
$\boldsymbol{\nu}_1$	2954	2956	2951	2956	V 26	149	148	105	92
ν,	2951	2955	2950	2955	v	93	67		71
ν ₃	2922	2916	2908	2919	11				
ν	2904	2919	2901	2916	а"				
ν	2859	2856	285 9	2852	v_{28}	2940	29 18	2922	2917
V ₆	2859	2852	2837	2855	v 79	2918	2913	2897	2913
ν,	1452	1452	1438	1451	ν ₃₀	2859	2855	2837	2854
V ₈	1439	1436	1427	1425	V 31	2859	2852	2837	2851
v	1347	1353	135 9	1350	V	1460	1447	1439	1440
v 10	1332	1333	1350	1342	ν ₁₁	1438	1441	1429	1434
V 11	1265	1247	1274	1268	ν_{34}	1379	1383	1359	1357
ν_{12}	1252	1245	1238	1231	V 35	1350	1359	1350	1350
ν_{13}	1199	1200	1186	1200	V 36	1294	1316	1310	1323
v_{14}	1145	1137	1150	1160	ν_{37}	1285	1273	1301	1317
V 15	1066	1071	1029	1042	V 38	1202	1204	1163	1170
v_{16}	996	999	1000	1007	V 10	1146	1138	1150	1156
ν_{17}	988	986	996	999	V 40	1076	1076	1128	1130
ν_{18}	885	879	865	864	ν_{41}	1063	1064	1066	1059
V 19	820	817	809	810	van	950	960	947 ·	954
V 20	727	731	716	705	V 43	895	898	861	860
V 21	653	656	593	592	ν_{aa}	790	793	809	800
ν_{22}	430	430	488	492	ν_{45}	460	465	465	463
ν_{23}	421	426	459	455	V 46	260	268	300	322
ν_{24}	322	321	345	349	V 47	234	234	260	258
ν_{25}	237	235	285	286	ν_{48}	145	129	126	104

Observed^a and calculated^b fundamental frequencies for *trans*-1,4-bromoiodocyclohexane

^aWhen possible, frequencies are taken from solution spectra. ^bSee footnotes to Table 5.

band. Although the present compounds also have intense IR and Raman bands around 1000 cm^{-1} , these are frequently not pure ee or aa bands, but often have contributions from both conformers. This region therefore has limited diagnostic value for the *trans*-1,4-dihalocyclohexanes.

The vibrational bands in the region $800-500 \text{ cm}^{-1}$ considered as C-X stretching bands (X is a halogen) are particularly useful in distinguishing conformations in linear and cyclic halogenated hydrocarbons, and a particular notation has been developed for this purpose [18]. These bands are very sensitive to the chemical and geometrical environment within the molecule since they are not simply localized C-X stretching modes, but are mixed with various skeletal stretching and bending vibrations.

In Table 7 are collected $v_{11}(a_g)$ and $v_{45}(b_u)$ for DCC [1], DBC and DIC, and $v_{20}(a')$ and $v_{21}(a')$ for CBC, CIC [2] and BIC. PED calculations [13] suggest that these modes all have substantial contributions from C—X stretching,

	<i>trans-</i> 1,4-Dihalo- cyclohexane			Monohalo- cyclohexane ^a					
	ee	aa	Diff.	Subst.	e	a	Diff.		
DCCp									
V 45	782	756	26						
ν ₁₁	726	648	78						
Av.			52	Cl	731	684	47		
DBC ^c									
V 45	738	728	10						
V 11	674	611	63						
Av.			37	Br	687	658	29		
DIC ^e									
v 45	703	707	—4						
v_{11}	631	581	5 0						
Av.			23	I	657	642	15		
CBCd									
ν_{20}	765	743	22						
ν_{21}	694	627	67						
Av.			45	$\frac{1}{2}(Cl + Br)$			38		
CICd									
V 20	755	730	25						
u 21	663	614	49						
Av.			37	$\frac{1}{2}(Cl + I)$			31		
BIC ^c									
V 20	727	716	11						
ν_{21}	653	593	60						
Av.			36	$\frac{1}{2}(Br + I)$			22		

The "C-X stretching modes" (cm⁻¹; X = halogen) in the *trans*-1,4-dihalo- and monohalocyclohexanes

^aFrom ref. 15. ^bFrom ref. 1. ^cThis work. ^dFrom ref. 2.

although in some cases other modes have a larger contribution than those selected (e.g. ν_{46} (b_u) for aa at 561 cm⁻¹ in DCC) [13]. It may be seen that these fundamentals are at higher frequencies for the ee than for the aa conformers, the only exception being ν_{45} for DIC. The wavenumber difference between the ee and aa bands is invariably largest for ν_{11} (a_g) in DCC, DBC and DIC, and for ν_{21} (a') in CBC, CIC and BIC, which "corresponds" to ν_{11} in the former group. The arithmetic mean (average in Table 7) is compared to the corresponding "C—X stretch" of the monohalocyclohexanes [15, 19]. Our PED calculations [13] reveal that the C—X stretch contribution for the monohalocyclohexanes is also divided between several normal vibrations. It appears that the "average" wavenumber differences between the ee and aa conformer bands in the *trans*-1,4-dihalocyclohexanes agree reasonably well with the corresponding differences in the monohalocyclohexanes.

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REFERENCES

- 1 O. H. Ellestad and P. Klaeboe, J. Mol. Struct., 26 (1975) 25.
- 2 T. Woldback, O. H. Ellestad, J. E. Gustavsen and P. Klaeboe, J. Mol. Struct., 62 (1980) 9.
- 3 E. Halmøy and O. Hassel, Z. Phys. Chem., Abt. B, 15 (1932) 472; 16 (1932) 234.
- 4 P. Klaeboe and T. Woldbaek, Appl. Spectrosc., 32 (1978) 588.
- 5 A. B. Remizov and L. M. Sverdlov, Dokl. Akad. Nauk SSSR, 179 (1968) 1389.
- 6 K. Kozima and T. Yoshino, J. Am. Chem. Soc., 75 (1953) 166.
- 7 R. J. Abraham and Z. Rosetti, J. Chem. Soc., Perkin Trans. 2, (1973) 582.
- 8 T. Yoshino, Bull. Chem. Soc. Jpn., 27 (1954) 592.
- 9 A. Allen, V. Fawcett and D. A. Long, J. Raman Spectrosc., 4 (1976) 285.
- 10 J. E. Gustavsen, P. Klaeboe and H. Kvila, Acta Chem. Scand., Sect. A, 32 (1978) 25.
- 11 S. D. Christian, J. Grundnes and P. Klaeboe, Appl. Spectrosc., 30 (1976) 227.
- 12 S. D. Christian, J. Grundnes and P. Klaeboe, J. Am. Chem. Soc., 97 (1975) 3864.
- 13 T. Woldback, C. J. Nielsen and P. Klaeboe, J. Mol. Struct., in press.
- 14 P. Klaeboe, C. J. Nielsen and T. Woldbaek, J. Mol. Struct., in press.
- 15 P. Klaeboe, Acta Chem. Scand., 23 (1969) 2641.
- 16 H. Horntvedt and P. Klaeboe, Acta Chem. Scand., Sect. A, 29 (1975) 528.
- 17 P. Klaeboe, Acta Chem. Scand., 25 (1971) 695.
- 18 C. Altona, Tetrahedron Lett., 19 (1968) 2325.
- 19 M. Rey-Lafon, C. Rouffi, M. Camiade and M. T. Forel, J. Chim. Phys. Phys. Biol., 67 (1970) 2030.