

## The conformations, phase transitions and vibrational spectra of bicyclohexyl

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**Abstract**—The i.r. spectra of bicyclohexyl as a liquid under atmospheric pressure and as three solid crystalline phases obtained under high pressure and ambient temperature were recorded. Low temperature i.r. spectra of the amorphous and of two crystalline phases were obtained. Raman spectra of the liquid, including semiquantitative polarization data, and of two crystalline phases at low temperatures were obtained.

Bicyclohexyl apparently exists in the *ee* conformation as a mixture of *anti* ( $C_{2h}$  symmetry) and *gauche* ( $C_2$  symmetry) around the C–C pivot bond. In the high pressure crystal formed at 1–2 kbar (phase I HP) both conformers were present and one series of dichroic measurements of a single crystal revealed complete order. At 2–8 kbar (phase II HP) only the *anti* conformer, and above 15 kbar (phase III HP) only the *gauche* conformer were present in the crystals; the three phases I HP, II HP and III HP were reversibly formed by pressure variations. By cooling, the phases II LT and III LT containing *anti* and *gauche* conformers, respectively, were reversibly formed, but phase I LT was not observed with certainty. An additional low temperature phase believed to be metastable was formed by annealing the amorphous solid from 90 K to ca 130 K. The differential thermal analysis (DTA) data suggested variations in the phase transition temperatures and enthalpies depending upon the thermal history of the sample.

A nearly complete assignment of the i.r. and Raman spectra to *anti* and *gauche* (both of *ee*) conformers were made, supported by a force constant calculation.

### INTRODUCTION

A number of 4-(4'-*n*-alkylcyclohexyl)-cyanocyclohexanes, which form nematic (and sometimes additional smectic) liquid crystals, have recently become commercially available. These liquid crystals have low optical anisotropies and no u.v. absorption bands above 220 nm. Therefore, they are much better suited as solvents for u.v.-visible spectroscopic studies of oriented guest molecules than the more conventional liquid crystals based upon the biphenyl skeleton [1].

We have recently studied the order parameters of a number of anthraquinone dyes as solutes in oriented cyanobicyclohexyl nematogens [2]. Moreover, the i.r. dichroic spectra of three cyanobicyclohexyls have been investigated in different phases [3]. In order to interpret the i.r. and Raman spectra of these compounds, it was advantageous to make an independent study of the "backbone" of these nematogens, bicyclohexyl. Particularly, we wanted to investigate the conformational equilibria of bicyclohexyl and if possible analyse the i.r. and Raman spectra. These results and those obtained earlier for substituted cyclohexanes, including cyano- [4], isocyano- [4], *trans*-1,4-dicyano- [5] and isocyanatocyclohexane [6] and on alkyl cyclohexanes [7] should be of considerable importance for the understanding of cyanobicyclohexyl liquid crystals [3].

Some scattered papers dealing with bicyclohexyl have been published, including certain i.r. [8, 9],

Raman [9] and far i.r. bands [10] of the liquid, proton NMR data [11–13], depolarized Raman scattering [14], fluorescence [15] and molecular mechanics calculations [16, 17]. The main problems still remain unanswered: (1) which conformers are present in the liquid and in what abundance, (2) which conformer(s) is (are) present in the crystal and (3) analyses of the vibrational spectra and assignment of bands to the proper conformer.

During the investigation of bicyclohexyl a number of very interesting and highly unexpected features were observed in the high pressure and in the low temperature crystal spectra. Differential thermal analysis (DTA) revealed different peaks in the 160–280 K range on cooling and on heating. Moreover, the DTA peaks of the heating curves were different if the sample had been initially cooled to 160 or 200 K. Various reversible phase transitions were found with increasing pressure at ambient temperature and with decreasing temperatures at atmospheric pressure. These phase transitions involved a complete reversal of the conformation present. One high pressure phase had a remarkable tendency to form single crystals. Each of these features are rare and have to the authors' knowledge never before been observed in the case of simple hydrocarbons. Taken together, these results reveal that bicyclohexyl is a hydrocarbon with most unusual properties in the solid state.

### EXPERIMENTAL

The sample of bicyclohexyl was a commercial product from EGA-Chemie. A GC analysis revealed the compound to be better than 99.5% pure, and the sample was therefore studied without further purification.

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The i.r. spectra were recorded on a Perkin-Elmer model 225 spectrometer ( $4000\text{--}200\text{ cm}^{-1}$ ) and on an evacuable FTIR spectrometer (Bruker model 114C) between  $800$  and  $50\text{ cm}^{-1}$ . The Raman spectra were obtained with a Dilor RT 30 triple monochromator Raman spectrometer, interfaced with the Aspect 2000 minicomputer of the Bruker spectrometer. The  $514.5\text{ nm}$  line of a Spectra Physics Series 2000 argon ion laser was used for excitation.

Conventional sealed i.r. cells for liquids and solutions with windows of KBr, CsI and polyethylene were employed at ambient temperature. Three types of i.r. cryostats were used: (A) a commercial steel cryostat from Beckmann in which the inner sealed cell with windows of AgCl was cooled with acetone-dry ice, (B) a glass cryostat in which the vapour was sprayed on a CsI window at  $90\text{ K}$ , subsequently annealed to higher temperatures and recooled to  $90\text{ K}$ , (C) a far i.r. cryostat with an inner window of silicon, outer windows of polyethylene, fitted into the vacuum tank of the Bruker spectrometer and operated at  $90\text{ K}$  like (B).

A high pressure diamond anvil cell (DAC) with type IIa windows was interfaced with a  $4\times$  beam condenser from Perkin-Elmer. The sample was placed into a hole of  $0.4\text{ mm}$  diameter in a bronze spacer and controlled visually in a polarization microscope between each recording.

An ordinary fluorescence cell of glass was used for the Raman polarization measurements at ambient temperature. Two Raman cryostats were used: (D) the sample was filled into a glass capillary of  $3\text{ mm}$  inner diameter, surrounded by a Dewar [18], cooled with cold  $\text{N}_2$  gas and used in the range  $210\text{--}290\text{ K}$  with  $90$  and  $180^\circ$  illumination, (E) the sample vapour was condensed on a copper finger at  $90\text{ K}$  for ca  $2\text{ h}$  and the initial amorphous sample was annealed as in (B).

Differential thermal analysis was recorded on a Perkin-Elmer model DSC 1B, cooled with liquid nitrogen, and calibrated against benzene. Heating and cooling curves were observed separately, the former started at  $170$  or at  $200\text{ K}$  using  $2$  or  $4^\circ/\text{min}$  temperature rates.

## RESULTS

The i.r. spectrum of liquid bicyclohexyl in the  $4000\text{--}100\text{ cm}^{-1}$  range is given in Fig. 1, while the corresponding Raman spectrum is shown in Fig. 2. Various low temperature i.r. spectra in three frequency regions recorded at  $265\text{ K}$  (phase II LT, solid line) and at  $240\text{ K}$  (phase III LT, dashed line) obtained by cooling the liquid in cryostat (A) are given in Figs 3–5. When the sample was reheated from  $240$  to  $265\text{ K}$  the solid curve spectrum was obtained once more. In cryostat (B) the initially formed deposit, obtained by shock freezing the vapour on the CsI window at  $90\text{ K}$ , gave an amorphous substance rather similar to the liquid spectrum (Fig. 1). When the sample was annealed to ca  $150\text{ K}$  it acquired a frosty appearance. After recoiling to  $90\text{ K}$  the solid line spectra of Figs 6 and 7 were obtained. If the sample was subsequently annealed to  $200\text{ K}$  and recooled to  $90\text{ K}$  the dashed lines of Figs 6 and 7 were observed. As is apparent, the latter spectra are similar to the dashed line spectra of

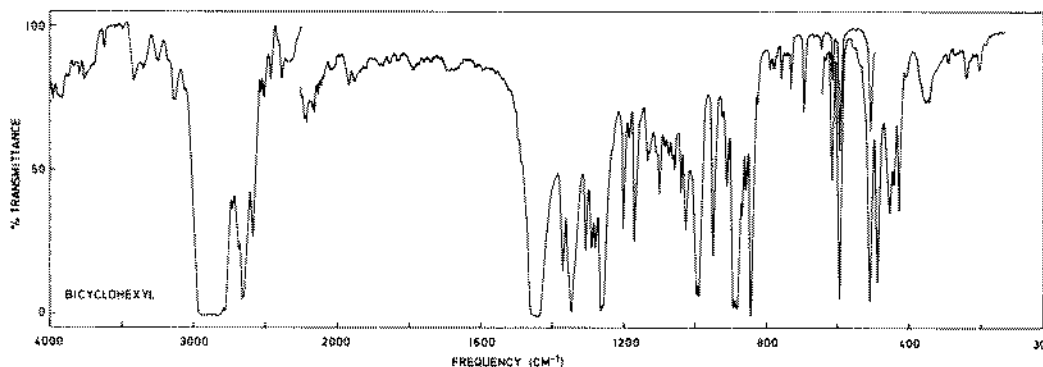


Fig. 1. The i.r. spectrum ( $4000\text{--}100\text{ cm}^{-1}$ ) of liquid bicyclohexyl ( $\text{C}_{12}\text{H}_{22}$ ).

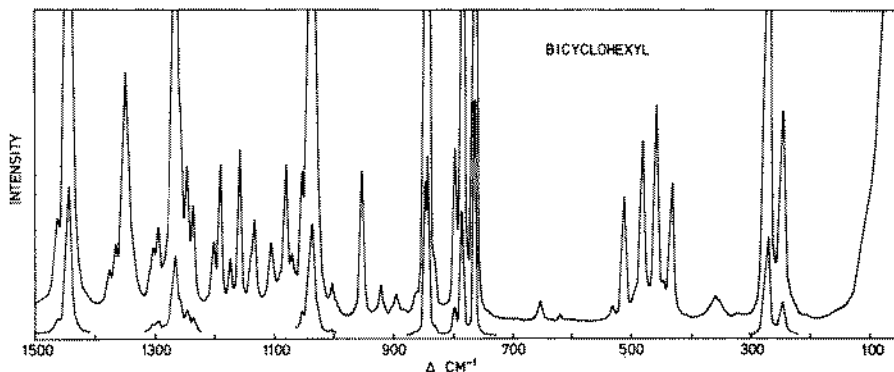


Fig. 2. The Raman spectrum of liquid bicyclohexyl below  $1500\text{ cm}^{-1}$ .

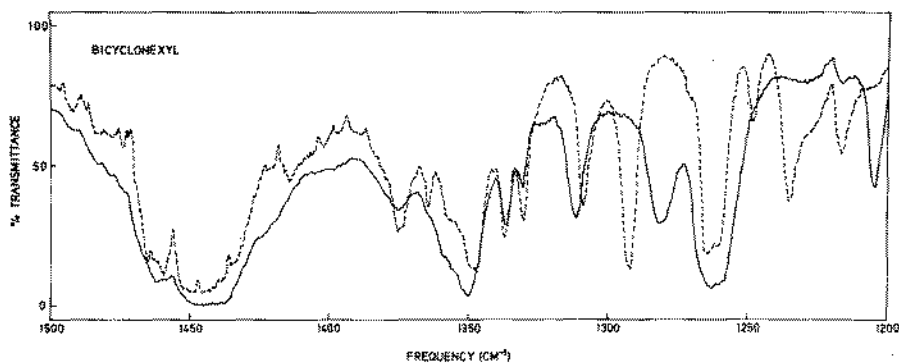


Fig. 3. The i.r. spectra of bicyclohexyl at 265 K (solid line, phase II LT) and at 240 K (dashed line, phase III LT) in the  $1500\text{--}1200\text{ cm}^{-1}$  range.

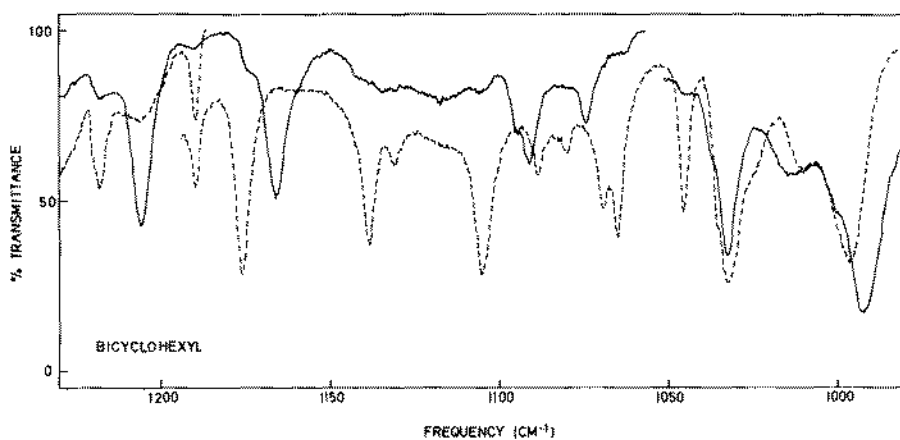


Fig. 4. The i.r. spectra of bicyclohexyl (see Fig. 3) in the  $1230\text{--}980\text{ cm}^{-1}$  range.

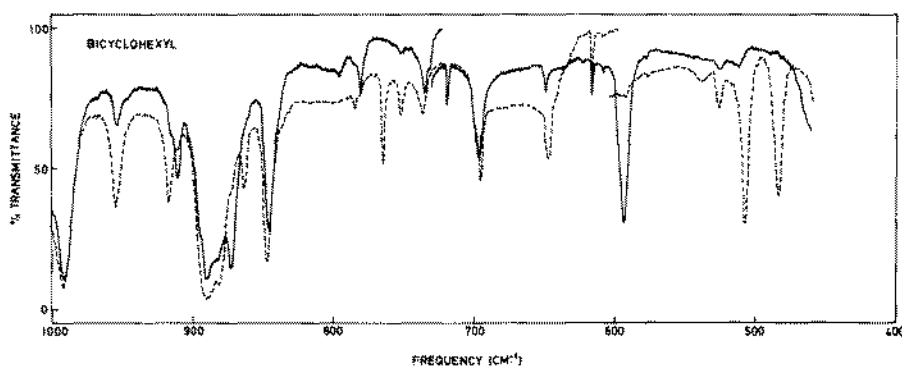


Fig. 5. The i.r. spectra of bicyclohexyl (see Fig. 3) in the  $1000\text{--}450\text{ cm}^{-1}$  range.

Figs 3–5 (phase III LT). After this phase was formed we could not get the solid curves of Figs 6 and 7 back by heating, indicating that this phase is metastable.

Raman spectra of the crystalline substances at 265 K (phase II LT, solid line) and at 240 K (phase III LT,

dashed line), recorded in cryostat D by cooling the liquid are shown in Figs 8 and 9. Also in this cryostat the phase transition between the phases II LT and III LT appeared completely reversible. When the vapour was shock frozen on the copper finger at 90 K (cryostat

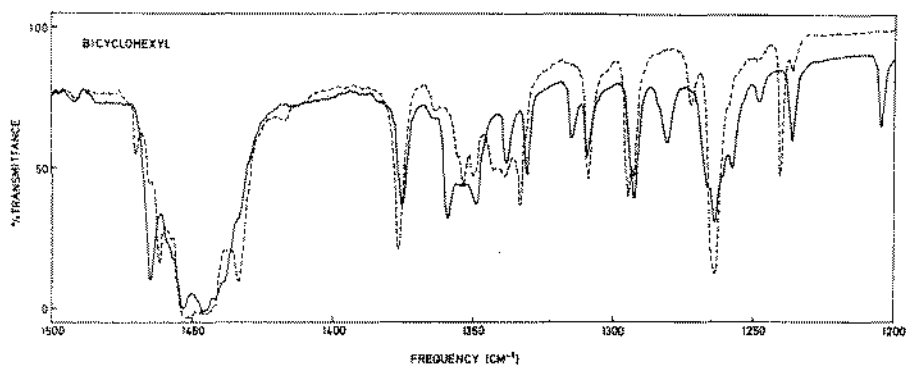


Fig. 6. The i.r. spectra ( $1500\text{--}1200\text{ cm}^{-1}$ ) of bicyclohexyl at 90 K, annealed to 150 K (solid line) and to 200 K (dashed line).

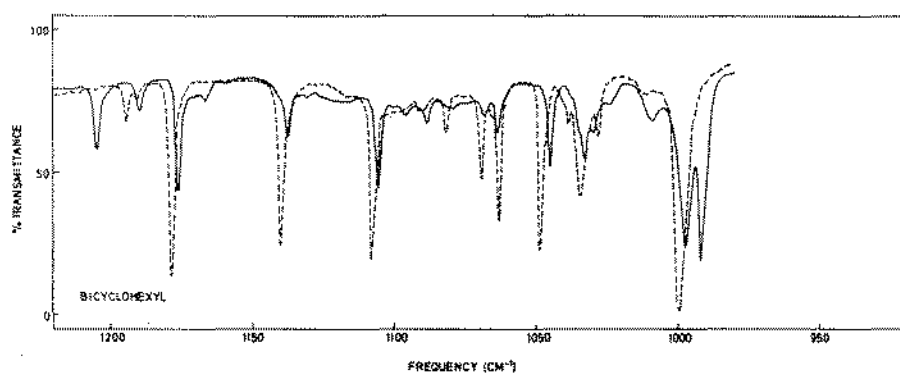


Fig. 7. The i.r. spectra ( $1230\text{--}980\text{ cm}^{-1}$ ) of bicyclohexyl at 90 K, annealed to 150 K (solid line) and to 200 K (dashed line).

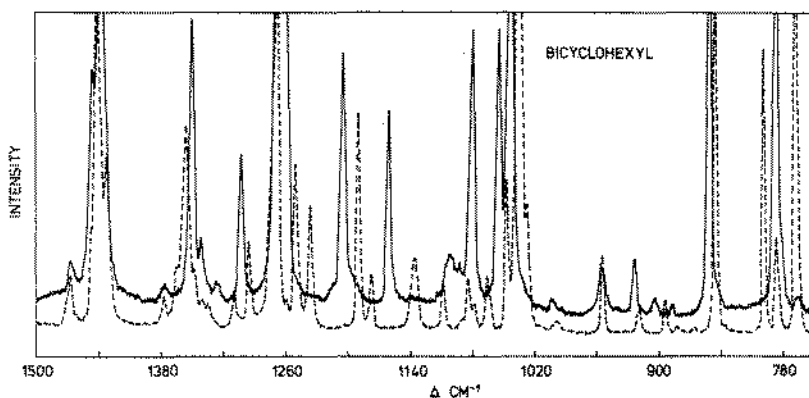


Fig. 8. Raman spectra of bicyclohexyl at 265 K (solid line, phase II LT) and at 240 K (dashed line, phase III LT) in the  $1500\text{--}760\text{ cm}^{-1}$  range.

E) a Raman spectrum of an amorphous solid was obtained. After annealing to ca 150 and 200 K two different Raman curves were obtained quite parallel to the i.r. curves of Figs 6 and 7.

Two DTA heating curves for bicyclohexyl are shown in Fig. 10(a) and (b). In (a) the sample was cooled to

230 K before the heating cycle started, whereas in (b) the sample was initially cooled to 175 K. Because of the discrepancies between the curves the thermal analysis was repeated several times giving reproducible results. A cooling curve is shown in Fig. 10(c).

Two examples of high pressure i.r. spectra are

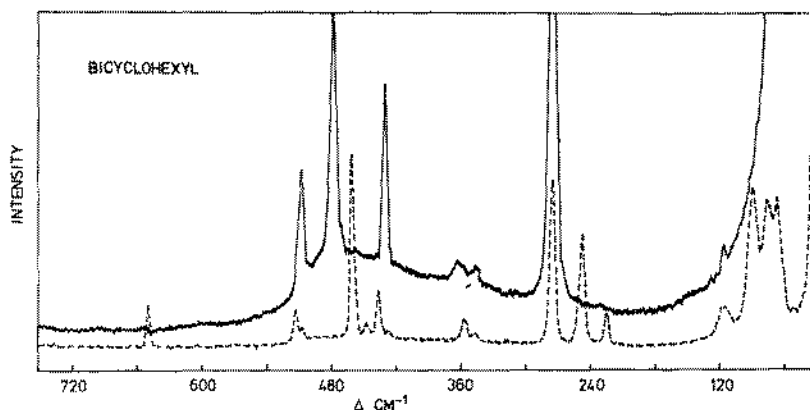


Fig. 9. Raman spectra of bicyclohexyl at 265 K (solid line) and at 240 K (dashed line) below  $740 \text{ cm}^{-1}$ .

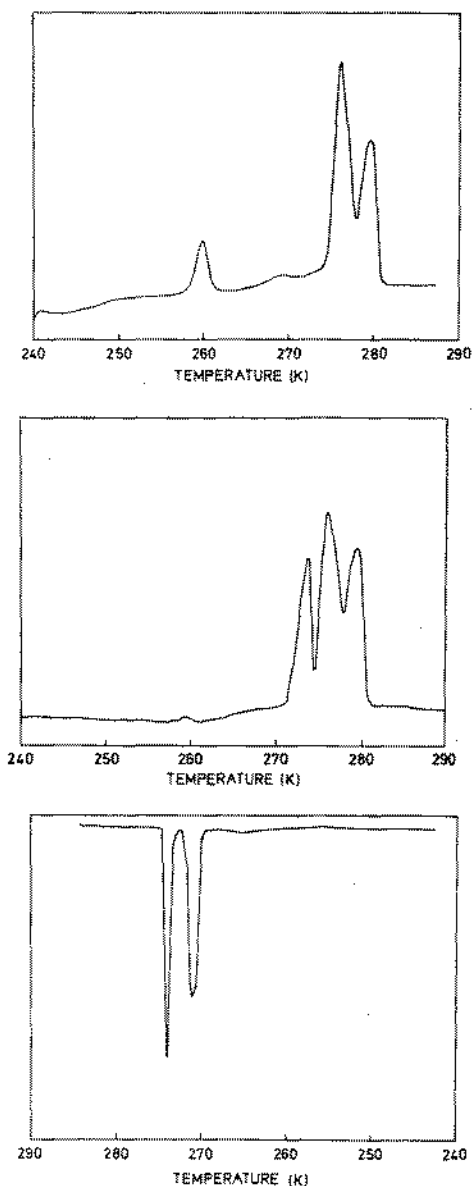


Fig. 10. Differential thermal analysis curves for bicyclohexyl: (a) heating curve, sample initially cooled to 230 K; (b) heating curve, sample initially cooled at 175 K; (c) cooling curve.

depicted in Figs 11 and 12. Both these spectra show the first high pressure phase formed at ca 2 kbar when the liquid was compressed. Initially, a polycrystalline substance was formed, making faintly coloured crystallites in a polarization microscope (phase I HP). When the sample stood overnight at ambient temperature and ca 2 kbar pressure, a single crystal was frequently (but not always) formed. The dichroic spectra of Figs 11 and 12 were obtained with two different single crystals. They had apparently quite different orientations relative to the diamond anvils, making the dichroic spectra very dissimilar. If the polarizer was removed, however, the spectra of Figs 11 and 12 were much more similar and both were fairly like that of the liquid (Fig. 1). The dichroic ratios in Fig. 11 indicate that by chance the transition vectors of a large number of the fundamental vibrations are oriented parallel or perpendicular to the i.r. electric vectors. The dichroic data for this single crystal are listed in Table 1.

When the pressure in the DAC was increased to 4–6 kbar a phase transition was clearly seen in the microscope. The crystallites formed (phase II HP) had colours in the polarization microscope which were brighter than those of phase I HP, but they did not form a single crystal. Infrared spectra of this high pressure phase (phase II HP) were quite similar to those of phase II LT (Figs 3–5, solid line). Therefore, the spectra are not reproduced for the sake of brevity, but the observed frequencies are listed in Table 1. The observed band maxima in the high pressure spectra are usually shifted towards higher frequencies compared with the corresponding low temperature bands. In addition the signal/noise ratio and spectral resolution is poor in the DAC spectra due to the 0.4 mm sample size.

The pressure was increased further to ca 15–20 kbar and a new phase transition was clearly seen in the microscope. Strongly coloured needle shaped crystallites were formed which had no tendency towards forming single crystals. The i.r. spectra of these crystals (phase III HP) were quite similar to those of phase III LT (Figs 3–5, dashed line; Figs 6, 7, dashed line) and the frequencies are listed in Table 1. If the pressure was gradually reduced, the phases II HP and I HP were

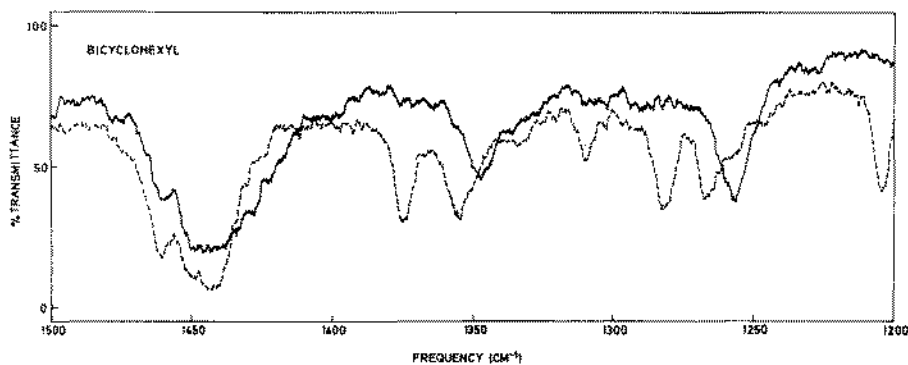


Fig. 11. High pressure i.r. dichroic curves of bicyclohexyl as a single crystal (phase I HP) at ca 2 kbar, ambient temperature. (Data listed in Table 1.)

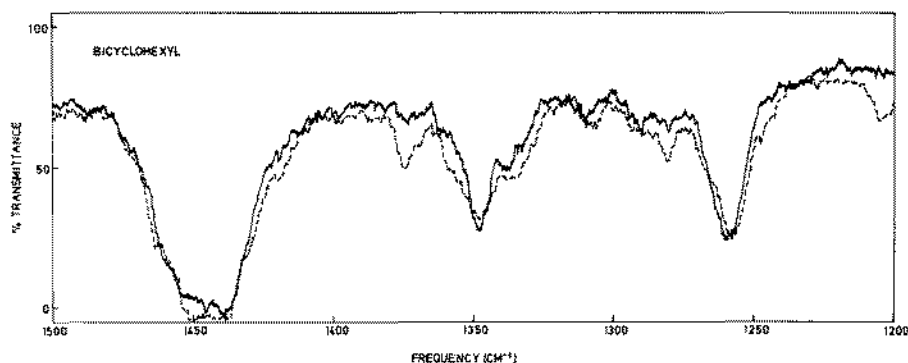


Fig. 12. High pressure i.r. dichroic curves of bicyclohexyl as a single crystal (phase I HP) at ca 2 kbar, ambient temperature; crystal oriented differently from that of Fig. 11.

formed again (taking the known hysteresis of the DAC into account [19]). Thus, the three observed high pressure phases I HP, II HP and III HP are reversibly formed at room temperature.

A large bulk of the observed i.r. data are listed in Table 1, while the corresponding Raman data are given in Table 2. Due to the large amount of experimental observations, severe restrictions were made in the presentation. Therefore, only certain representative spectra are reproduced and the i.r. and Raman data concerning the metastable, low temperature phase (*cf.* Figs 6 and 7) have not been included in Tables 1 and 2.

#### DISCUSSION

##### *Low temperature phases*

The DTA measurements clearly reveal that bicyclohexyl has a number of phase transitions, although not all of them are clearly understood. Most interesting, however, is the fact that some of these phase transitions involve complete conformational changes, making bicyclohexyl a very special molecule. The weak peak in Fig. 10(a) at 259 K is attributed to the III LT-II LT phase transition, II LT-I LT is at 274 K while the melting occurs at 278 K. An additional very weak maximum is observed at 269 K. In Fig. 10(b), the 259 K

peak is now very weak, while three equally intense maxima are observed at 272, 274 and 278 K. Possibly, the weak maximum at 269 K in Fig. 10(a) corresponds to the 272 K peak in Fig. 10(b). Upon cooling, the DTA curve exhibits two sharp peaks at 274 and 271 K and a very weak maximum at 265 K, showing hysteresis effects at the cooling rate employed (2°/min).

The phase transition at 259 K (III LT-II LT) is definitely reversible as observed during the spectral recordings although the 259 K peak is lacking at the cooling rate used in obtaining Fig. 10(c). It appears from Figs 3-5, 8 and 9 that the spectra changes completely at this temperature and, to be discussed below, phase III LT contains molecules in the *gauche* and II LT the *anti* conformer. Moreover, the i.r. and Raman spectra recorded at 90 K and annealed to 200 K appeared similar to those obtained at 240 K, not only concerning conformations, but in the low frequency lattice mode region as well. Therefore, it seems likely that no further 1st order phase transitions occur between 259 and 90 K.

The additional phase transitions at 269 and/or 272 and 274 K are very close to the melting point at 278 K. An uncontrolled heating occurs in the intense i.r. beam from the global source as well as in the focussed laser beam, both of which cannot easily be observed by the

Table 1. Infrared spectral data\* for bicyclohexyl

Liquid	Crystalline†		Crystalline‡				Assignment§	
	II LT 265 K	III LT 240 K	I HP⊥ 1 kbar	I HP∥ 1 kbar	II HP 5 kbar	III HP 20 kbar	C <sub>2h</sub>	C <sub>2</sub>
			1475 vw¶					
1462 sh	1463 w	1463 w	1461 m	1461 m¶	1464 m		{ 53 78	12-16, 61-65
1447 s	1453 m 1444 s	1453 s 1443 s	1450 s 1445 s	1450 s¶ 1444 s¶	1445 s		{ 54 79	
1436 sh	1436 sh		1434 w	1434 sh 1431 sh			80	
			1428 w } 1423 w } 1418 sh }	1426 sh				
					1418 w 1398 vw 1394 vw			
1373 w	1375 w	1374 m		1375 s	1374 w	1376 m	55	{ 17 18
	—	1365 w	1364 w					{ 67
1357 sh	1358 w			1355 s	1360 sh	—	81	{ 19 68
					1352 s	1350 m	56	
1349 m	1351 m	1349 m		1347 m				20
					1349 sh	1347 m		{ 57 82
1337 vw	1337 m	1337 m			1337 m	1338 m		
1332 sh		1330 w		1333 w	—	1331 m		{ 79 70
	1312 m	—			1312 m		58	
1310 m				1310 m				
		1309 w				1309 m		{ 22 71
			1302 w	1302 w			Comb.	Comb.
1293 m	—	1292 m		1292 m	—	1293 s		72
1291 w**								
1282 w	1281 m	1280 vw		1277 m	1283 m	—	83	23
	1265 sh	1264 s	1266 m	1266 sh	1263 s	1266 s	84	24
1265 s	1262 s	—						
1258 m	1259 sh	1259 m		1246 w	1257 sh	1261 m	59	73
	—	1248 vw		1240 vw	—	1249 vw		74
1228 w	—	1235 m	1241 vw			1238 w		25
	—	1228 w	1231 vw			1234 vw		75
			1226 w					
1217 w	—	1217 m						26
1205 w	1205 w	—		1204 s	1206 m	—	85	
1191 w	—	1189 vw			—	1191 w		27
1174 m	—	1176 s	1173 w	1174 m	—	1177 s		76
1169 sh	1166 m	—	1169 w		1166 s	—	60	
1160 vw	—			1161 w				77
1139 w	—	1138 m	1139 w	1141 vw	—	1139 m		28
1133 w	—	1130 vw				—		29
1114 vw	1118 vw		1119 vw	1119 vw			61	
1106 m	—	1104 s	1107 w		—	1107 m		78
1092 w	1091 w	—		1090 w	1092 vw	1090 vw	62	79
				1087 w				
1080 w	—	1079 w	1079 w		1076 vw	—		30
	1075 w	—					{ 63 86	
1069 w	—	1068 w	1066 w	1067 vw	—	1070 vw		31
1064 w	—	1064 m	1062 w¶	1064 w	—	1067 m		{ 80 32
			1057 w					
1045 m	—	1045 w	1044 w	1046 m	—	1048 w		33
1030 m	1032 m	1032 m	1033 w		1033 s	1033 m	87	81
1028 sh			1028 m			1027 w		
999 s	—	996 s		998 s	—	998 s		82
992 s	991 s	—	991 m	992 m¶	991 s	—	88	
953 s	—	955 s	953 s		954 w	956 m		34
929 w**			930 w					
		918 m			—	918 m		{ 35 83
915 m	—		915 vw	915 m				
	911 w	—			912 w	—	64	

Table 1. (Contd.)

Liquid	Crystalline†		I HP,⊥ 1 kbar	Crystalline‡		III HP 20 kbar	Assignment§	
	II LT 265 K	III LT 240 K		I HP ‖ 1 kbar	II HP 5 kbar		C <sub>2h</sub>	C <sub>2</sub>
895 s	—	893 sh	891 s	—	—	896 sh	—	84
886 s	886 s	890 s	887 s	887 w	886 s	890 s	65	36
882 s	—	881 s	882 s	883 w	—	882 s	—	85
873 w	873 m	—	—	873 s	873 s	—	89	—
862 vw	—	864 w	—	—	—	864 w	—	37
846 s	—	848 s	848 w	849 s	—	848 s	—	38
796 w	845 m	—	—	—	847 s	—	90	—
796 w	796 vw	—	—	—	—	—	—	87
785 w	783 m	785 w	780 w	780 w	783 w	784 vw	91	39
—	—	765 m	—	—	—	764 m	—	40
763 m	760 m	760 sh	760 w	760 w	—	—	66	88
—	—	752 sh	—	—	—	—	—	—
736 w	736 w	738 sh	—	—	732 w	—	—	—
—	719 w	720 w	—	—	—	—	—	—
699 s	699 s	700 s	—	—	698 w	698 w	—	—
667 w	667 m	667 m	—	—	—	—	—	—
651 w	—	647 w	—	—	—	646 w	—	89
619 w	616 w	616 w	—	—	—	—	—	—
597 m	593 s	—	597 w¶	597 w	594 m	—	92	—
577 w	577 w	577 w	—	—	—	—	—	—
512 m	—	508 m	512 w	510 vw	—	507 w	—	41
490 m	—	484 m	—	—	—	484 w	—	90
—	—	—	459 w	—	—	—	67	42
456 w	—	—	452 w	—	452 sh	—	93	—
445 w	—	—	—	—	—	—	—	91
430 w	—	—	—	—	—	—	—	—
413 w	—	—	—	—	419 w	—	—	92
—	—	—	—	—	395 m	—	94	—
374 sh	—	—	390 vw	—	392 w	—	—	—
—	—	—	—	—	383 w	—	—	—
354 w	—	—	353 vw	—	375 m	—	—	—
348 w**	—	—	—	—	354 w	—	—	44
—	—	—	309 w	309 w	302 w	—	95	—
296 w	—	—	295 w, br	295 w, br	—	—	—	—
—	—	—	—	—	289 vw	—	—	—
277 w	—	—	—	—	279 w	—	—	45
245 w	—	—	256 w	256 m	253 vw	—	68	46
—	—	—	—	—	—	—	—	—
233 sh	—	—	242 w	245 w	241 w¶	235 w	—	94
—	—	—	—	—	—	223 w	—	—
208 w	—	—	218 w	219 w	209 w	—	—	47
191 vw	—	—	—	210 w	195 sh	—	—	—
—	—	—	—	—	191 w	—	Lattice	—
—	—	—	—	—	169 m	—	—	95

\*Data above 1500 cm<sup>-1</sup> have been omitted.

†Low temperature crystalline phases, II LT and III LT.

‡High pressure crystalline phases at ambient temperature: I HP, II HP and III HP, ⊥ and ‖ denote dichroic spectra (cf. Fig. 11).

§C<sub>2h</sub> and C<sub>2</sub> are conformer symmetries (a) and (b) (cf. Table 3); numbers refer to fundamental modes.

¶Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; (—) vanishing bands.

¶¶Stronger of polarized components.

\*\*Possibly belonging to the *ea* conformer (c) (cf. Table 3).

thermocouple. Many attempts were made to record i.r. and Raman spectra in the interval between 269 K and melting. We do believe that there is one or possibly two phases in this temperature range which are identical to the phase I HP (Figs 11 and 12) in which both conformers are present. Therefore, the Raman spectrometer was set at 843 or 248 cm<sup>-1</sup> and the i.r. spectro-

meter at 895 cm<sup>-1</sup> on bands absent in *anti* but present in *gauche*, as conformational probes when the temperature was gradually raised from ca 265 K. However, no *gauche* bands at these wavenumbers were ever observed before the sample melted, suggesting no phase transitions involving conformational changes. Additional spectra will be recorded at this temperature



Table 2. Raman spectral data\* for bicyclohexyl

Liquid	Crystalline		Interpretation†		
	II LT 265 K	III LT 240 K	C <sub>2h</sub>	C <sub>2</sub>	
1464 mP‡	1467 w	1465 m 1459 w	8 9,32	} 12-16 61-65	
1445 s	1446 m	—	10,33		
1443 sh	1443 sh	—			
—	1440 s	—			
—	1437 s	—	11		
—	1429 sh	—			
1376 wD	1378 vw	1412 sh 1378 w	34		66 17
1365 wP	—	1364 w	}		18
—	—	1358 m			67
—	—	—			19
—	—	—		68	
1350 mD	1350 s	1348 s	35	20	
1341 sh	1342 w	—	36	21	
1335 sh	—	—	—	69	
1332 sh	1331 vw	1331 w	12	70	
1326 sh§	—	—	}	71	
1304 shD	—	1309 w			22
1302 shP?	1303 m	—	}	72	
—	—	—			37
1296 w	—	1293 m	—	23	
1283 sh	—	1272 m	—	24	
1266 mD	1269 s	1268 s	38	24	
1258 sh	1263 sh	—	14	73	
1253 w	1259 m	—	15	74	
1247 wD	—	1249 s	—	25	
1236 wP	—	1239 s	—	27	
1202 wD	1205 m	1205 vw	39	Comb.	
1192 mP	—	1188 s	—	76	
1175 wD	—	1181 m	—	77	
1160 mD	1161 m	1160 w	16	28	
1139 shP	—	1141 s	—	29	
1134 mP	—	1136 s	—	78	
1125 vw§	—	—	—	79	
1107 wD	1102 w	1106 w	17	80	
—	1092 w	1093 w	40	Comb.	
1081 mD	—	1084 sh	—	30	
—	1080 m	1078 s	41	} 31, 32	
1072 shD	—	1067 s	—		
—	1055 m	—	42	80	
1054 wD	—	1048 s	—	33	
—	1044 s	—	18	81	
1038 sP?	—	1039 s	—	Comb.	
—	—	1027 m	—	82	
1010 wP?	1009 vw	1016 sh	Comb.	Comb.	
1004 vw	—	1000 w	—	34	
955 mP	955 w	954 m	19	} 35 83	
926 wD	924 w	922 w	43		
—	—	—	—		
894 wP	892 vw	—	}	36	
—	—	—		44	
883 vw	—	878 m	—	85	
864 vw	—	864 w	—	37	
849 sP	851 s	—	21	38	
843 sP	—	845 s	—	86	
832 w	—	836 sh	—	87	
799 mD?	—	799 s	—	39	
787 sP	786 s	789 m	22	Comb.	
783 sh	779 sh	779 sh	45	} 40 88	
766 sP	—	767 s	—		
653 wD§	—	—	—	—	

Table 2. (Contd.)

Liquid	Crystalline		Interpretation†	
	II LT 265 K	III LT 240 K	C <sub>2h</sub>	C <sub>2</sub>
646 wD	—	648 m	—	89
627 vwP§	—	—	—	—
531 vwP§	—	—	—	—
513 mP	508 m	512 sh 507 m	23	41
493 shD?§	—	—	—	—
487 mP	478 s	473 vw	24	90
459 mP	—	457 s	—	42
445 wD	—	446 w	—	91
433 mD	430 m	} 433 m 426 w	46	} 43 92
358 vwP	363 vw		25	
350 wD	—	354 w 351 sh	—	93 44
—	346 vw	—	47	—
275 shD	275 s'	—	}	48 26
271 sP	—	276 s		
248 mP	—	248 s	—	46
227 w	—	225 w 214 vw	—	94 47
—	128 vw	—	27	—
—	115 w	112 w	Lattice	Lattice
—	—	88 s	—	} 48 96
80 sh	76 w	—	—	
—	—	65 s	—	49
—	57 sh	—	Lattice	—

\*Data above 1500 cm<sup>-1</sup> have been omitted.

†C<sub>2h</sub> and C<sub>2</sub> are conformer symmetries (a) and (b) (cf. Table 3); numbers refer to fundamental modes.

‡Abbreviations: s, strong; m, medium; w, weak; v, very; P, polarized; D, depolarized; sh, shoulder; (—) vanishing bands.

§Possibly belonging to the *ea* conformer (c) (cf. Table 3).

interval in the future using more sophisticated temperature control (a Displex unit from Air products combined with the FTIR spectrometer which has a lower i.r. emission than the Perkin-Elmer spectrometer).

In the older proton NMR study [11] of bicyclohexyl no conformational change was observed in the temperature range 143–403 K, probably because of low resolution. The fluorescence spectrum [15], however, showed a very distinct drop in intensity followed by a subsequent enhancement within a few degrees between 273 K and melting (278 K). A red shift from 215 to 227 nm in the fluorescence (blue shift of the absorption spectrum) was simultaneously observed [15]. The authors suggest tentatively a possible conformational change [15], in accordance with our assumption that a phase I LT similar to the phase I HP should contain both conformers. However, the phase transition at 259 K involving a complete conformational change from *anti* to *gauche* was not observed [15] in the fluorescence spectra. The "metastable" phase of Figs 6 and 7 seems to contain both the *anti* and the *gauche* conformers, suggesting that in spite of the frosty appearance this is merely a mixture of amorphous and phase III LT.

### High pressure phases

The DAC has the great advantage that melting, solidification and solid–solid phase transitions can be observed visually in a polarization microscope and the spectra subsequently recorded in u.v., i.r. and Raman spectrometers. Moreover, the high pressure crystals obtained at room temperature can sometimes consist of molecules in another conformer than the low temperature crystal, as observed for six *trans*-1,4-dihalocyclohexanes [20], *trans*-1,2-bromochlorocyclohexane [21] and isocyanatocyclohexane [6]. In other cases crystallization can be obtained under high pressure, but is unsuccessful at low temperatures as observed for isocyanatocyclohexane [4] and 1,1,2-trichlorotrifluoroethane [22].

In bicyclohexyl the liquid crystallized at ca 2 kbar to form phase I HP. The crystallites initially formed or the single crystal had identical i.r. spectra containing both *anti* and *gauche* conformers, suggesting that the phase might be plastic with large internal molecular motions. Cyclohexane as well as certain monosubstituted derivatives like fluoro- [23], chloro- [24], cyano- [4], isocyano- [4] and isocyanatocyclohexane [5] all have plastic high pressure phases, appearing without colours in a polarization microscope, since the plastic crystals generally are isotropic (have a cubic structure) [25]. Plastic crystals are generally formed from globular molecules [25], whereas bicyclohexyl (in the *ee* conformation) is more rod like. Also the melting entropy of 6.1 J/mol K for bicyclohexyl [15] is higher than for most plastic crystals [25].

Smectic to isotropic phase transitions have energies close to this value. Both smectic A, B and C phases can have a homogeneous texture [26]. These phases will show a high degree of order and viewed through a polarization microscope they will give colour effects. Certain 4-(4'-alkyl-cyclohexyl)-cyanocyclohexanes give smectic B phases, and it is shown that the conformational distribution will be the same in this phase as in the isotropic liquid [3]. Other bicyclohexyl derivatives like 4,4'-dialkyl- [27], 4-cyanoethyl-4'-alkyl- [28] and 4-alkanoyl-4'-alkyl-bicyclohexane [29] all show smectic phases. On the other hand it should be noted that the distinction between highly ordered smectic phases and plastic crystals with restricted rotations is rather blurred and is a subject for discussion [30].

The following features are characteristic for phase I HP: (1) both the *anti* and *gauche* conformers are present, (2) the crystallites have faint colours in the microscope, (3) a single crystal was easily formed, (4) complete molecular order (dichroic ratio) relative to the DAC could be achieved. As an hypothesis phase I HP might be tetragonal rather than cubic, explaining the faint crystallite colours. Since the barrier to internal rotation around the pivot C–C bond is quite low [17] bicyclohexyl may convert between *anti* and *gauche* in phase I HP, forming essentially a semiplastic phase. In a recent study of  $\text{CH}_3\text{C}(\text{CH}_2\text{Cl})_3$  [31] it was

observed that the conformational equilibrium was temperature dependent in the plastic phase as in vapours and liquids, revealing a completely dynamic equilibrium.

A static conformational ratio independent of temperature and pressure within phase I HP cannot be completely ruled out, however. In principle *anti* and *gauche* molecules in a simple stoichiometric ratio (like 1:1 or 1:2) might take definite positions in the unit cell. An example of this type was recently observed for  $\text{H}_2\text{Si}-\text{C}\equiv\text{C}-\text{SiH}_2-\text{CH}_2-\text{SiH}_2-\text{C}\equiv\text{C}-\text{SiH}_2-\text{CH}_2$  in which the triclinic unit cell has one chair and two boat molecules [32]. This alternative might explain the complete molecular order (the dichroic ratio) of phase I HP better than the dynamic model.

The close similarity between the i.r. spectra of phase II HP obtained in the 4–6 kbar range and those of phase II LT observed around 265 K strongly suggests that these phases are identical. A close inspection of the i.r. and Raman lattice modes in the low frequency region would definitely confirm this hypothesis. However, experimentally, these observations are difficult to carry out with the high pressure sample.

In the 15–20 kbar i.r. spectra (phase III HP) all the spectral features appeared identical to those of the 240 K spectra (phase III LT). Again, the data strongly suggest that these two phases are identical, and the descriptions LT and HP will therefore be omitted from phases II and III in the following. No additional phase transitions were observed visually or in the spectra when the pressure was increased to 100 kbar. Similarly, no phase transitions occurred (see above) when the temperature was reduced to 90 K.

### Conformers present

Bicyclohexyl can in principle exist in six possible conformers as listed in Table 3. It is well established that the equatorial conformer is the more stable in the vapour and liquid states of all monosubstituted cyclohexanes [33]. The lowest energy difference of 1.00 kJ/mol [34] was observed for cyanocyclohexane, which unlike other monosubstituted cyclohexanes crystallizes in the axial conformer [4]. The energy difference between *ee* and *ea* in bicyclohexyl was estimated [12] to be 9.2 kJ/mol. Thus, very small amounts of the *ea* conformer and practically none of the *aa* conformer should be present at room temperature. Models reveal that the *ea* conformer, *gauche* (d), and the *aa*, *gauche* (f), are sterically impossible (Table 3). Therefore, it can be assumed *a priori* that only the *ee anti* and *gauche* are abundant, possibly in addition to very small amounts of *ea anti* (c).

According to recent molecular mechanics calculations [16, 17] bicyclohexyl maintains a chair–chair conformation during rotation around the C–C central bond. The barrier was estimated to 11.7 kJ/mol [16], changed to 20.71 kJ/mol the following year with a slightly modified force field [17]. The *anti* conformer was supposedly the more stable [16], whereas *gauche*

Table 3. Possible staggered conformers of bicyclohexyl

Cyclohexane conformer	Dihedral angle	Dihedral conformer	Symmetry	Multiplicity	Designation
<i>ee</i>	0	<i>Anti</i>	$C_{2h}$	1	a
<i>ee</i>	120	<i>Gauche</i>	$C_2$	2	b
<i>ea</i>	0	<i>Anti</i>	$C_s$	2	c
<i>ea</i> *	120	<i>Gauche</i>	$C_1$	4	d
<i>aa</i>	0	<i>Anti</i>	$C_{2h}$	1	e
<i>aa</i> *	120	<i>Gauche</i>	$C_2$	2	f

\*Sterically highly improbable.

was slightly more stable in the latest version [17]. Thus, the molecular mechanics calculations are very uncertain and highly dependent upon small variations in the force fields adopted. However, it can probably be concluded that the energy difference between the *anti* ( $C_{2h}$ ) (a) and *gauche* ( $C_2$ ) (b) both of conformer *ee* (Table 3) is very low. This is in perfect agreement with the present results. When the energy difference between the conformers is negligible, the conformation present in the crystal may be completely determined by crystal forces, as observed in this study of bicyclohexyl.

The i.r. and Raman spectra of the liquid compared with those of phase II and III are in perfect agreement with the assumption that there are two conformers in the liquid (and in phase I HP), but one in each of the phases II and III. A quick glance at the spectra of phase II reveals far fewer bands than in those of phase III. Closer analyses of the spectra show beyond doubt that phase II consists of the *anti* conformer with mutual exclusion between i.r. and Raman bands. In phase III the i.r. bands have Raman counterparts and *vice versa* characteristic for *gauche*. It cannot be completely ruled out that conformer (c) (*ea*, *anti*) might be present in small amounts in the liquid. Thus, the very weak polarized Raman band at  $531\text{ cm}^{-1}$  (Table 2) vanishes in both phases II and III and might be interpreted as a (c) conformer band. The same is found for a very weak Raman band at  $1125\text{ cm}^{-1}$ , a weak depolarized band at  $653\text{ cm}^{-1}$  and a depolarized shoulder at  $493\text{ cm}^{-1}$ .

In the i.r. spectra weak bands were observed at 1291, 929 and  $430\text{ cm}^{-1}$  of the liquid phase which could not be detected in the crystalline phases. The  $929\text{ cm}^{-1}$  band, however, has a counterpart at 930 in the I HP spectrum.

#### Spectral interpretation

The phase transitions combined with the very unusual conformational changes make the spectral interpretation of bicyclohexyl a possible task in spite of the inherent complexity in assigning 96 fundamentals of two conformers simultaneously. A normal coordinate analysis (see below) was carried out for the *anti* and *gauche* conformers, and these results were of great help for the interpretations. The fundamentals assigned for *anti* and *gauche* are listed in Tables 4 and 5, respectively, together with the results of the force constant calculations.

Obviously, there will be several cases of overlap

between i.r. and Raman bands of *anti* and *gauche* as seen from the frequent simultaneous presence of bands in phase II and in phase III spectra (Tables 1 and 2). Also, accidental degeneracies between modes of *a* and *b* species of *gauche* and  $a_g$ ,  $b_g$ ,  $a_u$  and  $b_u$  of *anti* do occur. With 10  $\text{CH}_2$  groups in the molecule, conformational overlap and accidental degeneracies will be numerous for the  $\text{CH}_2$  asymmetric stretch (around  $2920\text{ cm}^{-1}$ ),  $\text{CH}_2$  symmetric stretch (around  $2850\text{ cm}^{-1}$ ),  $\text{CH}_2$  scissor ( $\sim 1450\text{ cm}^{-1}$ ) and wag ( $\sim 1350\text{ cm}^{-1}$ ). To a lesser extent frequent accidental degeneracies were previously observed in the spectra of cyclohexane [35] and the *trans*-1,4-dihalocyclohexanes [20]. No attempts were made to assign the overlapping  $\text{CH}_2$  stretching and in part the  $\text{CH}_2$  scissoring vibrations in Tables 1, 2, 4 and 5. Most of the observed i.r. (Table 1) and Raman bands (Table 2) are assigned to fundamentals of conformers *anti* (a) and *gauche* (b). The remaining observed bands are considered as combination bands or overtones. With the large number of fundamentals (96), many alternative explanations can be proposed for these bands.

The conformation of an observed band is first established from the crystal phases II and III spectra. These results should agree with the mutual exclusion in *anti* and the coinciding i.r. and Raman bands in *gauche*. The polarized Raman bands should belong to  $a_g$  of *anti* or *a* of *gauche*, while the depolarized bands should be of  $b_g$  or *b*. Obviously, these criteria have limited significance in the case of overlapping bands with polarized and depolarized components. In a few cases bands of the *gauche* conformer are observed in the i.r. or in the Raman spectrum only, due to the generally low intensity of the bands.

The relation between the bands observed in the liquid phase and in either one of the crystalline phases is mostly straightforward, except for the Raman band at  $276\text{ cm}^{-1}$  in III LT which corresponds to the liquid band at  $271\text{ cm}^{-1}$ , while the band at  $275\text{ cm}^{-1}$  in II LT also appears at  $275\text{ cm}^{-1}$  in the liquid phase.

As is apparent from Fig. 1 the i.r. bands below  $450\text{ cm}^{-1}$  have very low intensities. For this reason a very thick layer of bicyclohexyl was deposited on the inner window of the far i.r. cryostat. A reasonably good far i.r. spectrum of the amorphous phase was obtained at 90 K, but spectra of the crystal phases II and III were of poor quality because of very high and tilted background. Also the high pressure spectra of the

Table 4. Observed and calculated fundamental frequencies for the *anti* ( $C_{2h}$ ) conformer (a) of bicyclohexyl\*

$\nu$	Observed†	Calculated
<i>a<sub>g</sub></i>		
1		2935
2		2928
3		2926
4		2908
5		2857
6		2855
7		2855
8	1464	1456
9	1445	1456
10	1443	1452
11	1429‡	1417
12	1332	1341
13	1302	1317
14	1258	1256
15	1253	1235
16	1160	1166
17	1107	1115
18	1038	1049
19	955	944
20	894	899
21	849	841
22	787	786
23	513	511
24	487	463
25	358	336
26	275	249
27	128‡	152
<i>b<sub>g</sub></i>		
28		2930
29		2924
30		2856
31		2855
32	1445	1456
33	1443	1453
34	1376	1384
35	1350	1357
36	1341	1344
37	1302	1319
38	1266	1250
39	1202	1203
40	1092‡	1111
41	1081	1089
42	1054	1076
43	926	936
44	894	899
45	783	789
46	433	451
47	350	388
48	275	221
<i>a<sub>u</sub></i>		
49		2930
50		2925
51		2856
52		2855
53	1462	1456
54	1447	1455
55	1373	1391
56	1349	1357
57	1337	1343
58	1310	1306
59	1258	1251
60	1169	1180
61	1114	1102
62	1092	1089
63	1075‡	1071
64	915	921

Table 4. (Contd.)

$\nu$	Observed†	Calculated
65	886	886
66	763	791
67	456	466
68	245	232
69		119
70		43
<i>b<sub>u</sub></i>		
71		2935
72		2928
73		2926
74		2905
75		2857
76		2855
77		2855
78	1462	1456
79	1447	1454
80	1436	1452
81	1357	1384
82	1337	1342
83	1282	1279
84	1265	1254
85	1205	1205
86	1075‡	1081
87	1030	1052
88	992	984
89	873	884
90	846	845
91	785	802
92	597	605
93	456	475
94	395‡	396
95	302‡	291
96		77

\*The fundamentals 1–7, 28–31, 49–52 and 71–77 ( $\text{CH}_2$  stretch) are highly overlapping and are not assigned explicitly.

†The  $g$  ( $a_g, b_g$ ) and  $u$  ( $a_u, b_u$ ) modes are liquid Raman and i.r. values, respectively, except when noted.

‡Crystal Raman or i.r. values.

phases I, II and III were uncertain below  $400\text{ cm}^{-1}$  because of the low intensities and the general low energy conditions of the DAC in this region. For these reasons the assignments are more uncertain in this region. This is particularly true for the *anti* conformer (a) bands of species  $a_u$  and  $b_u$ , which are not supported by the more reliable Raman data in this region.

No straightforward distinction can be made experimentally between the i.r. active *anti* modes  $a_u$  and  $b_u$ , since no vapour contours are available and the crystal structure of the phase I HP is unknown. Tentatively, the dichroic ratios listed in Table 1 (see Fig. 11) can be used as a clue. Thus, it appears that the  $a_u$  modes are polarized parallel and the  $b_u$  modes are polarized perpendicular in cases of no overlap. Among the *gauche* bands, the  $a$  modes are polarized parallel. Those bands of species  $b$  which can be clearly discerned show an even distribution with five being parallel and five perpendicularly polarized.

Table 5. Observed and calculated fundamental frequencies for the *gauche* ( $C_2$ ) conformer (b) of bicyclohexyl\*

$\nu$	Observed†	Calculated
<i>a</i>		
1		2935
2		2930
3		2928
4		2926
5		2925
6		2904
7		2857
8		2856
9		2855
10		2855
11		2855
12		1456
13		1456
14		1456
15		1453
16		1452
17	1373	1400
18	1365‡	1387
19	1349	1357
20	1349	1350
21	1337	1341
22	1310	1319
23	1282	1275
24	1265	1257
25	1236‡	1251
26	1217	1221
27	1191	1192
28	1139	1137
29	1133	1126
30	1080	1092
31	1069	1081
32	1064	1053
33	1045	1042
34	953	944
35	915	934
36	886	902
37	862	869
38	846	842
39	785	789
40	763	774
41	512	512
42	459‡	454
43	433‡	452
44	350‡	350
45	271‡	286
46	248‡	227
47	214§	217
48	80‡	77
49	65§	43
<i>b</i>		
50		2935
51		2930
52		2928
53		2926
54		2924
55		2905
56		2857
57		2856
58		2855
59		2855
60		2855
61		1456
62		1455
63		1455
64		1453
65		1452

Table 5. (Cont.)

$\nu$	Observed†	Calculated
66	1412§	1410
67	1365‡	1384
68	1349	1357
69	1337	1342
70	1332	1340
71	1310	1315
72	1293	1287
73	1258	1255
74	1247‡	1250
75	1228	1230
76	1174	1185
77	1160	1151
78	1106	1096
79	1092	1086
80	1064	1068
81	1030	1050
82	999	982
83	915	924
84	895	904
85	882	885
86	832‡	846
87	796	800
88	763	789
89	651	645
90	490	490
91	445‡	467
92	433‡	449
93	350‡	340
94	227‡	229
95	169	189
96	80‡	96

\*The fundamentals 1-16 and 50-65 ( $\text{CH}_2$  stretch and scissor) are highly overlapping and are not assigned explicitly.

†Liquid i.r. values except when noted.

‡Liquid Raman values.

§Crystal Raman values.

#### Force constant calculations

The standard valence force field for saturated hydrocarbons developed by SNYDER and SCHACHTSCHNEIDER [36] was employed for calculating the normal modes of vibration for the *ee anti* and *gauche* conformers of bicyclohexyl. As seen from Tables 4 and 5 the prediction of the vibrational spectrum is quite satisfactory, though an improvement in the overall agreement might be obtained by adjusting the torsional force constants in accordance with our results from the halogenated cyclohexanes [20]. However, this is of minor importance in the present context.

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