

The Conformation and Vibrational Spectra of Cyano- and Isocyanocyclohexane

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The IR spectra of cyano- and isocyanocyclohexane as liquids and as amorphous, plastic and crystalline solids at low temperatures were recorded in the region $4000-50\text{ cm}^{-1}$. High pressure (0–40 kbar) IR spectra of the neat samples were obtained in a diamond anvil cell at ambient temperature, and the dichroism of oriented crystalline high pressure crystals was measured. Raman spectra of the liquids, including polarization measurements, and of various low temperature solid phases were recorded.

Both compounds form a mixture of equatorial and axial conformers in the liquid state with nearly equal abundance of the two conformers. Unlike other monosubstituted cyclohexanes, cyanocyclohexane exists as *a*-conformer in the low temperature and high pressure crystals. Isocyanocyclohexane crystallizes in the *a*-conformation at high pressure, whereas both conformers were present in the low temperature solid phases. Plastic phases, with equilibria of *e* and *a* conformers, were observed for both molecules at low temperature as well as under high pressure.

A normal coordinate analysis was carried out for the two molecules, using a constrained valence force field analogous to the one derived for the *trans*-1,4-dihalocyclohexanes. Tentative assignments of the fundamentals belonging to both the *e* and *a* conformers are presented and compared with the results from the normal coordinate analysis.

The conformational equilibria of cyanocyclohexane (cyclohexanecarbonitrile, hereafter abbreviated CCN) and isocyanocyclohexane (CNC) have been carefully studied in solution by proton,¹⁻³ ^{13}C ⁴⁻⁶ and lanthanide-induced⁷ NMR spectroscopy and by equilibration^{8,9} technique. The more recent of these studies⁶ reveal ΔG° values equal to 0.214 (178 K) and 0.190 kcal/mol (180 K) for CCN and CNC,

respectively. These values are the lowest for 22 monosubstituted cyclohexanes studied except for cyclohexaneisocyanate⁶ ($\Delta G^\circ = 0.206$ kcal/mol). Unlike other monosubstituted cyclohexanes the equatorial and axial conformers of these compounds are therefore of nearly the same abundance at coalescence temperature (for CCN the *e*-conformer is determined to be of $54.5 \pm 3.1\%$ abundance⁷ at 303 K in CCl_4).

Some years ago we studied CCN by IR and Raman technique with special emphasis on the solid state.¹⁰ To our surprise the high pressure crystal consisted of molecules in the axial conformer whereas complete crystallization at low temperature was not achieved.

Later a systematic study of six *trans*-1,4-dihalocyclohexanes^{11,12} was completed by means of vibrational spectroscopy. The equatorial and axial conformers of these molecules were separately obtained in the solid state, the spectra interpreted in detail and an extensive force¹³ field was developed by the overlay technique. The force constants were transferred with negligible adjustments to the four monohalocyclohexanes^{14,15} and to *trans*-1,4-dicyanocyclohexane.¹⁶ It was decided to extend these studies to CCN and to CNC. New vibrational spectra for CCN were recorded in an extended frequency range. Corresponding data were measured for CNC which, apart from an IR survey spectrum,¹⁷ to our knowledge has not previously been studied by vibrational spectroscopy. Our results for both compounds will be given here, while ethynylcyclohexane ($\text{C}_6\text{H}_{11}\text{C}\equiv\text{C}-\text{H}$) which is isoelectronic with CCN and CNC will be treated in a forthcoming paper.¹⁸

EXPERIMENTAL

The samples of CCN and CNC were commercial products from Fluka and ICN, respectively. They were purified by fractional distillation under reduced pressure, and gas chromatographic analysis showed both to be better than 99% pure.

The IR spectra were recorded on a Perkin-Elmer model 225 spectrometer ($4000-200\text{ cm}^{-1}$) and on an evacuable fast scan Fourier transform spectrometer (Bruker 114 C) ($4000-50\text{ cm}^{-1}$). Raman spectra were obtained with a modified¹⁹ Cary 81 spectrometer, excited by a CRL model 52 G argon ion laser, using the 4880 and 5145 Å lines.

Conventional IR cells for liquids and solutions

were employed, having windows of KBr, CsI and polyethylene. Cryostats cooled by liquid nitrogen with windows of CsI and polyethylene were used in IR; a cooled copper plate was employed for the Raman studies. The temperatures were measured with iron-constantane thermocouples. The high pressure solids were studied in a diamond anvil cell with type II diamonds having spacers of brass and steel coupled to a P.-E. $4\times$ beam condenser.

The various high pressure solid phases were carefully inspected with a polarization microscope and the spectra mostly recorded with the P.-E. 225 equipped with a polarizer. Far IR and mid IR high pressure spectra at better resolution (2 cm^{-1}) were recorded with the Fourier transform spectrometer.

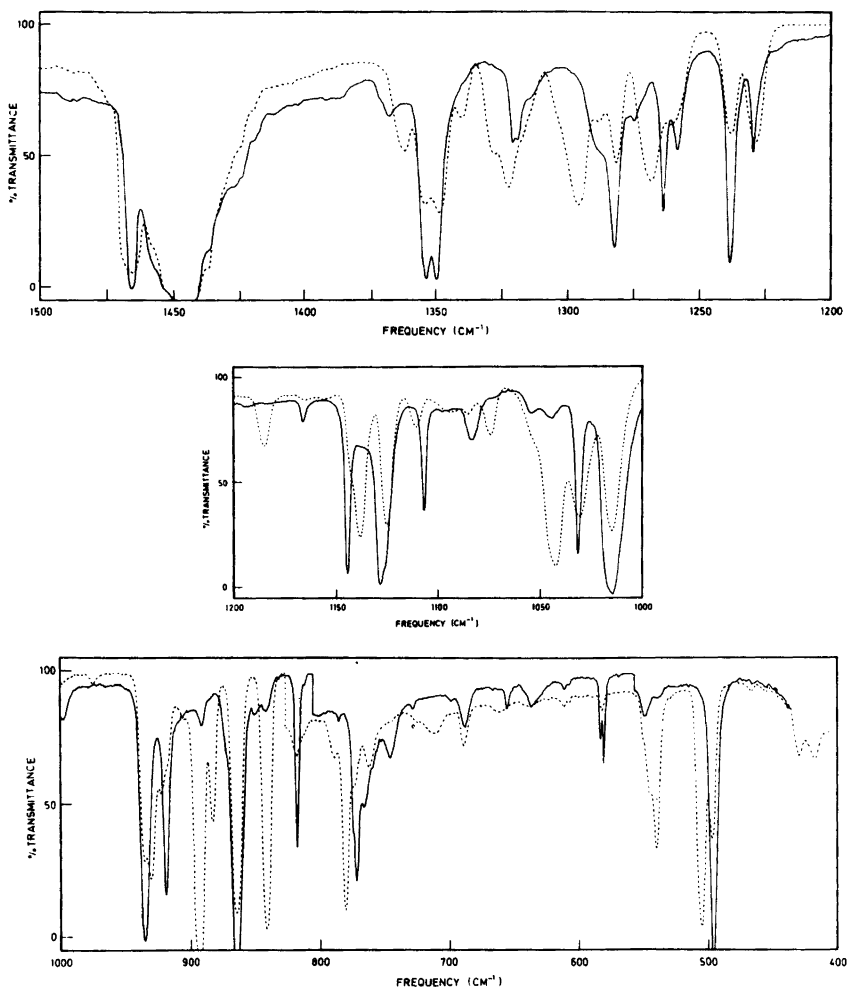


Fig. 1. Infrared spectra of cyanocyclohexane (CCN) as an amorphous solid (dotted curve) and as an anisotropic crystal annealed at 190 K (solid curve) both recorded at 90 K.

IR spectra of the CCN and CNC thiourea clathrates as nujol mulls were recorded using the technique described earlier.²⁰

RESULTS

The IR spectra of CCN as a liquid were presented in Ref. 10, the unannealed and annealed solids at 90 K are given in Fig. 1 and the various high pressure curves are shown in Fig. 2. Raman spectra of the

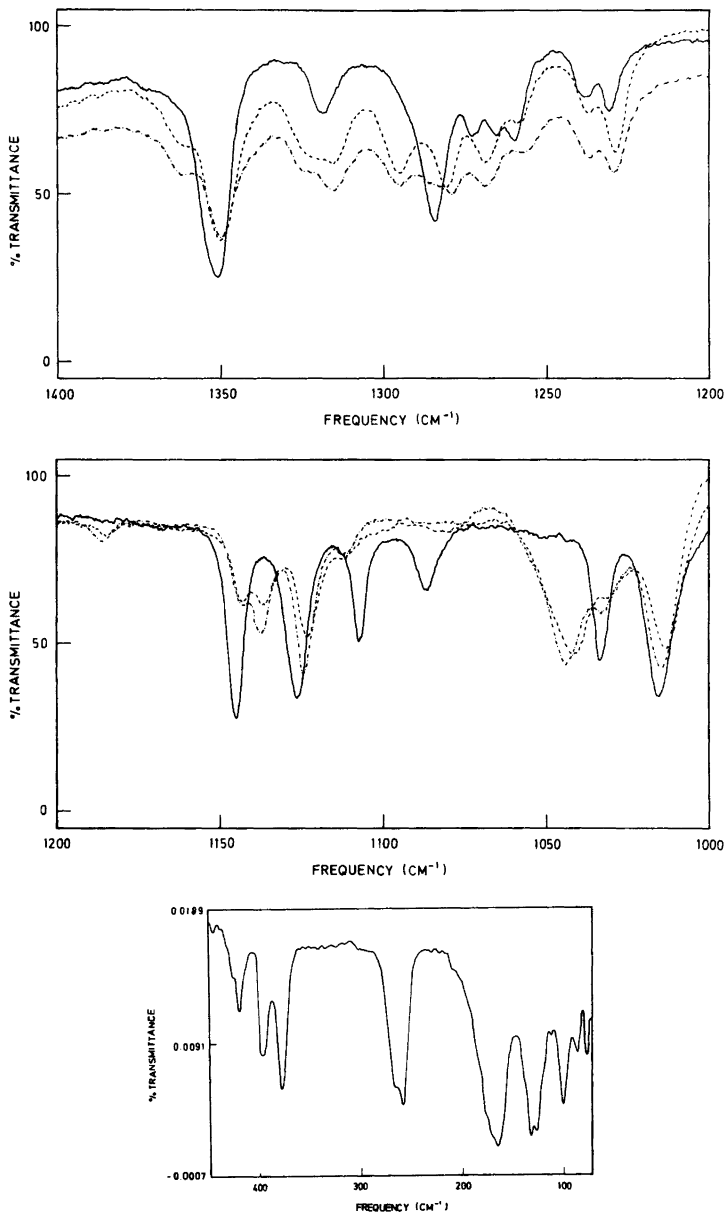


Fig. 2. Infrared spectra of cyanocyclohexane (CCN) in the diamond anvil cell as a liquid at negligible pressure (dashed-dotted curve), as a plastic phase at ca. 3 kbar pressure (dashed curve) and as an anisotropic crystal at ca. 18 kbar pressure (solid curve).

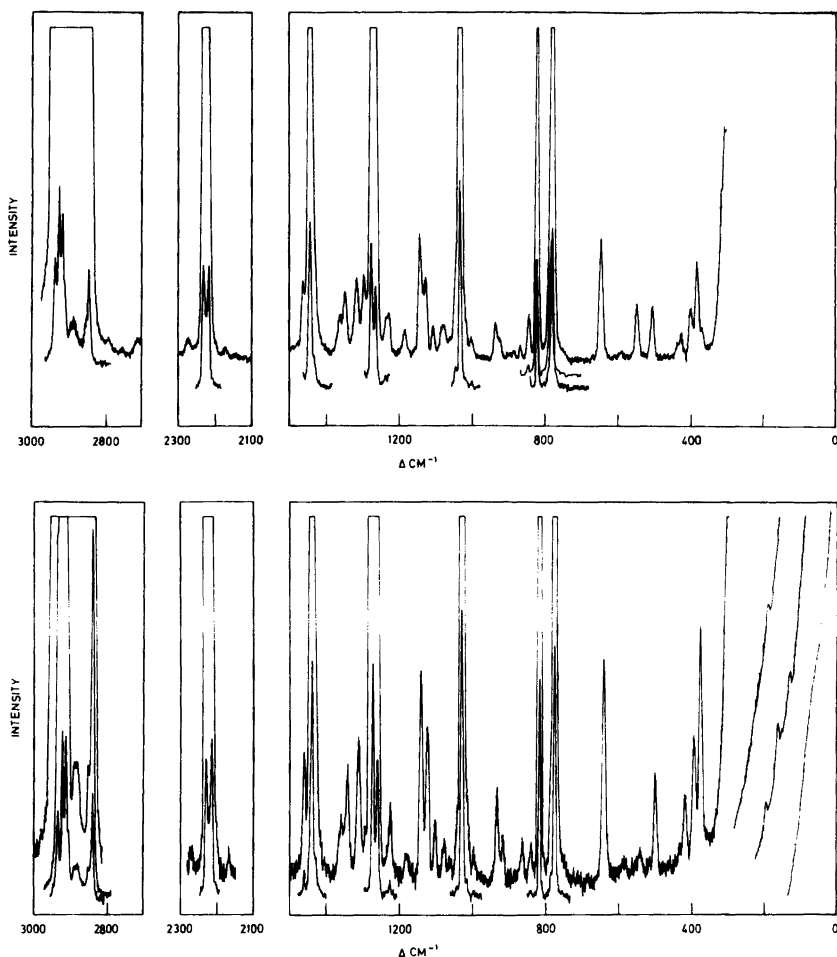


Fig. 3. Raman spectra of cyanocyclohexane (CCN) as an unannealed solid (top) and as a crystalline solid, annealed to 190 K (bottom) both recorded at 90 K.

unannealed and the annealed solids studied at 90 K are reproduced in Fig. 3. The IR and Raman spectra of CNC in the liquid state are given in Figs. 4 and 5, respectively. Low temperature IR curves for CNC appear in Fig. 6 whereas the high pressure spectra recorded with the diamond anvil cell are found in Fig. 7. The wave numbers of the observed IR and Raman bands for the two compounds are listed in Table 1 (CCN) and Table 2 (CNC). Our present CCN data are much more complete than those obtained previously;¹⁰ for CNC our results agree with the limited IR data reported.¹⁷

Cyanocyclohexane (CCN)

Low temperature solid. Earlier¹⁰ we did not achieve any simplification of the IR and Raman spectra upon solidification, although certain intensity variations were observed after annealing. A large effort was therefore invested in the present cooling of CCN, and various techniques were systematically applied. No success was obtained by cooling the sample from the liquid state. Shock freezing the vapour on a CsI window (IR) or copper block (Raman) at liquid nitrogen temperature and subsequent annealing for 1–2 h at 190 K finally caused crystallization. It appears from Figs. 1 and 3 that a number of bands present in the amorphous,

Table 1. Infrared and Raman spectral data^a for cyanocyclohexane (CCN).

Liquid	Amorphous		Crystalline		Assignments		
	Raman	IR 90 K	Raman 90 K	IR 90 K	Raman	equatorial	axial
3175 m ^c							comb.
2945 vs	2944 vs,P	2930 s,sh	2955 s 2944 vs 2933 vs		2955 s 2943 s 2933 s	v ₁ d' v ₂ d' v ₃ ,v ₃₀ d',d''	v ₁ d' v ₂ d' v ₃₀ d''
2905 s,sh	2927 s	2919 s,sh 2900 s	2927 m,sh 2914 m,sh 2904 m 2873 m,sh		2927 m,sh 2911 w 2904 w 2873 m,sh	v ₃ ,v ₃₀ d',d'' v ₃₁ d'' v ₄ d' v ₅ ,v ₆ ,v ₇ d' v ₃₂ ,v ₃₃ d'' comb.	v ₃₀ d'' v ₃₁ d',d'' v ₄ d' v ₅ ,v ₆ ,v ₇ d' v ₃₂ ,v ₃₃ d'' comb.
2860 vs	2860 vs,P	2950 s	2861 s		2859 s	v ₈ d' v ₉ d'	v ₈ d' v ₉ d'
2290 w	2283 w,sh	2286 vw	2285 vw,sh 2280 w		2285 vw,sh 2280 w	2 × v ₄₁ = 2286 A' v ₈ d' 2 × v ₁₇ = 2 × v ₄₂ = 2246 A' v ₉ d'	comb. 2 × v ₄₁ = 2286 A' v ₈ d' 2 × v ₁₇ = 2 × v ₄₂ = 2246 A' v ₉ d'
2240 s	2242 vs,P	2240 s	2244 s		2244 m	v ₁₀ d'	v ₁₀ ,v ₃₄ d',d''
1465 s,sh	2237 m	2230 s	2230 s		2228 m	v ₁₁ d'	v ₃₅ d'' v ₁₁ d'
1452 vs	1465 m,sh,P	1465 s	1470 w		1469 m	v ₁₂ d'	v ₁₂ ,v ₃₆ d',d''
		1457 m } 1454 s,sh } 1446 vs }	1457 m } 1454 s,sh } 1446 vs }		1459 m } 1459 s,sh } 1445 vs }	v ₁₃ d' v ₃₈ d'' v ₁₄ d'	v ₃₇ d'' v ₁₃ ,v ₃₈ d',d'' v ₁₄ d'
1448 s,sh	1447 s,D	1440 s,sh 1437 s,sh	1449 s		1447 vs	v ₁₁ d'	v ₁₁ d'
1405 vw		1365 m } 1362 m }	1436 w,sh		1436 m,sh	v ₁₂ d'	v ₁₂ ,v ₃₆ d',d''
1364 w	1365 w,D	1354 m	1371 vw } 1367 w }		1436 w	v ₃₆ d''	v ₁₂ ,v ₃₆ d',d''
1353 m	1353 w,D	1349 m	1354 s		1350 w	v ₁₃ d' v ₃₈ d''	v ₃₇ d'' v ₁₃ ,v ₃₈ d',d''
1327 w	1328 w,D	1341 w	1350 s		1350 w	v ₁₄ d'	v ₁₄ ,v ₃₉ d',d''
1318 w	1318 vw,P	1322 m } 1317 m }	1326 w,sh 1320 m } 1318 w }		1318 m		
			1319 m		1318 m		
			1320 w } 1315 m,sh }		1318 m		

Table 1. Continued.

1298 w	1299 s,D	1296 m	1299 m	*	*	*	$v_{39} a''$	comb. $v_{40} a''$ comb.
1287 w		1287 m						
1281 w		1281 m	1279 vs	1287 m,sh 1282 s	1284 s	1289 sI _⊥		
1270 w	1273 s,D	1268 m	1267 s	1275 w	1273 m	1276 wI _∥	$v_{15} a'$	
1258 w	1261 m	1260 w,sh		*	1265 m	1263 mI _∥	$v_{40} a''$	$v_{29} + v_{41} = 1268 A''$
1239 w	1241 w,D	1238 w	1240 w	1258 m	1260 m	1259 mI _⊥	$v_{16} a'$	
1231 w	1232 w,P	1229 m	1233 w,sh	1238 s } 1229 m }	1238 m } 1231 m }	1237 mI _∥ } 1227 mI _∥ }		$v_{16} a'$
1185 vw	1187 w,D	1185 w	1188 w	1194 vw	1188 w	*	$v_{41} a''$	comb.
		1165 vw		*	1166 w	1169 vw		comb. A''
		1155 vw		*	1144 s	1149 sI _⊥	comb.	
1143 w	1144 w,sh,D	1142 m,sh	1141 m	1144 s	1145 s	*	$v_{17} a'$	$v_{41} a'$
1136 w	1138 s,P	1138 m		*	1144 s	1131 sI _⊥ } 1127 sI _∥ }		$v_{17} v_{42} a', a''$
1123 m	1125 m,P	1125 s	1129 w,sh	1128 m,sh } 1126 vs }	1127 s	1105 mI _⊥		$v_{28} + v_{46} = 1111 A''$
1111 vw	1114 vs,sh	1110 w	1109 vw	1107 m	1107 m	1089 wI _⊥	$v_{42} a''$	
		1094 vw,sh		*	1087 m	*		$v_{43} a''$
1083 vw	1085 vw,sh,D	1084 vw	1087 w,sh	1083 w	1087 m	1036 mI _⊥ } 1032 mI _∥ }	$v_{44} a''$	comb.
1076 vw	1078 w,D	1079 w	1078 w	1054 w	1050 vw	1017 sI _∥	$v_{18} a'$	
1049 w,sh	1048 m,D	1053 w,sh	1047 s	1045 w	1043 vw	1036 mI _⊥ } 1032 mI _∥ }	v_{19}, a'	$v_{18}, v_{44} a', a''$
1041 s		1043 s		1032 s } 1029 m }	1033 s	1020 w		$v_{19} a'$
1031 m	1033 s,D	1030 m	1036 vs	1015 vs	1016 s	1002 vw		$v_{24} + v_{27} = 1009 A'$
1014 s		1014 s		997 w,sh	938 s	935 sI _∥	$v_{20} a'$	
935 m	1002 w,P	936 s	1005 vw	935 vs	938 s	*		
	932 m,P	931 m	935 m	*	935 s		$v_{45} a''$	
921 w,sh	921 vw,sh	923 w } 919 w }	922 vw,sh	919 s	924 m	929 sI _∥		
		905 vw		*	895 vw	*	$v_{29} + v_{47} = 913 A''$	
892 vs	892 w,D	896 vs	897 vw	892 w	895 vw	*	$v_{46} a''$	
882 vw, sh	882 w,P	884 w	886 vw	*	895 vw	*	$v_{21} a'$	
862 s	863 vw,P	865 vs	868 vw	873 w } 865 vs } 859 w }	869 s	870 s } 864 sI _⊥ }		$v_{21}, v_{46} a', a''$

Table 1. Continued.

839 s	842 s,P	841 s	844 m	842 vw	846 vw	*	823 m	844 vw	$\nu_{22} d'$	$\nu_{22} d'$
817 w	819 s,P	819 w	821 s	818 m	822 m		792 vw I_{\perp}	821 s	$\nu_{47} a''$	$\nu_{47} a''$
779 m	788 s,D?	789 w	779 s	*	786 vw			788 m	$\nu_{23} d'$	$\nu_{23} d'$
771 w	781 vs,P	781 m								
	774 s,P	774 w		$\left. \begin{matrix} 776 m \\ 772 s \end{matrix} \right\}$	$\left. \begin{matrix} 779 m \\ 772 s \end{matrix} \right\}$		778 m I_{\parallel}	778 vs		$\nu_{23} d'$
761 m		764 w		$\left. \begin{matrix} 766 w \\ 759 w \end{matrix} \right\}$	$\left. \begin{matrix} 762 w \\ 758 w \end{matrix} \right\}$		757 w I_{\parallel}	750 vw,sh	comb.	comb.
737 vw	743 w,sh	746 vw,sh		745 w	732 vw				$\nu_{25} + \nu_{28} = 753 A'$	$\nu_{25} + \nu_{28} = 753 A'$
689 w		725 vw		727 vw	690 w				$2 \times \nu_{27} = 742 A'$	$2 \times \nu_{27} = 742 A'$
638 vw	641 m,P	689 w	644 m	689 w	642 vw		640 vw	644 m	$\nu_{49} + \nu_{50} = 688 A'$	$\nu_{49} + \nu_{50} = 688 A'$
581 vw	583 vw	640 vw,bd		636 w	642 vw		583 w I_{\parallel}		$\nu_{24} d'$	$\nu_{24} d'$
		583 w	585 vw	$\left. \begin{matrix} 583 w \\ 581 w \end{matrix} \right\}$	585 w		550 vw		$\nu_{49} + \nu_{51} = 581 A'$	$\nu_{49} + \nu_{51} = 581 A'$
547 vw		551 w,sh		548 w	552 vw				$\nu_{48} a''$	$\nu_{48} a''$
		546 w,sh		*	*				comb.	comb.
540 w	542 s,P	541 m	544 m	*	*				ν_{24}, d'	ν_{24}, d'
505 w	506 m,P	506 m	506 w	*	*		503 s I_{\parallel}	502 w	$\nu_{25}, \nu_{48} d', a''$	$\nu_{25} d'$
496 w	499 w,sh,P	498 m	500 w,sh	496 vs	503 s				$\nu_{49} a''$	$\nu_{49} a''$
431 w	433 m,D	432 w	434 w	*	*				$\nu_{28} + \nu_{51} = 428 A''$	$\nu_{49} a''$
421 w	424 w,sh,D	422 w	423 w,sh	$\left. \begin{matrix} 425 w \\ 417 w \end{matrix} \right\}$	$\left. \begin{matrix} 427 w \\ 420 w \end{matrix} \right\}$		432 m } 419 w }	421 w	$\nu_{26} d'$	$\nu_{26} d'$
392 m ^f	389 m,bd,D	392 m	393 w	394 m	396 m		397 m	394 m		
385 m		389 m		386 vw	*					
371 s	373 m,P	376 m	378 m	$\left. \begin{matrix} 376 m \\ 373 s \end{matrix} \right\}$	379 s		381 s I_{\perp} } 376 m,sh I_{\perp} }	377 m	$\nu_{28} + \nu_{29} = 382 A'$	$\nu_{28} + \nu_{29} = 382 A'$
358 w,sh	359 s,P	362 w	364 m	*	*				$\nu_{27} d'$	$\nu_{27} d'$
317 vw							$2 \times \nu_{51} = 320 A'$		$2 \times \nu_{51} = 320 A'$	
267 m	269 m,D?	$\left. \begin{matrix} 273 s \\ 367 m \end{matrix} \right\}$	270 m	267 s	267 m,sh		278 s I_{\perp}	265 w	$\nu_{50} a''$	$\nu_{50} a''$
257 m	261 m,P	263 m,sh	260 m	259 s	258 s		265 m	265 w	$\nu_{28} a'$	$\nu_{28} a'$
238 vw,sh		241 w		*	*				$\nu_{50} a''$	$\nu_{50} a''$
157 s	162 s,D	$\left. \begin{matrix} 172 s \\ 155 s \end{matrix} \right\}$	163 m	162 vs	165 s			162 w	$\nu_{51} a''$	$\nu_{51} a''$
124 s	128 m,D	135 vs	125 m	135 vs	130 s			127 m	$\nu_{29} d'$	$\nu_{29} d'$

^a Weak bands outside the fundamental regions (4000–3100, 2800–2300, and 2000–1500 cm^{-1}) are omitted. ^b Plastic phase. ^c s, strong; m, medium; w, weak; v, very; sh, shoulder; P, polarized and D, depolarized. ^d I_{\parallel} and I_{\perp} dichroic measurements. ^e Asterisks indicate bands which are absent or with strongly reduced intensities in the crystal spectra. ^f Bands below 400 cm^{-1} were observed in benzene solution.

unannealed sample (dotted curves in Fig. 1) vanish in the annealed phase (solid curve). Moreover, the same bands disappeared in the earlier¹⁰ and present high pressure crystals and were assigned as equatorial bands. Therefore, CCN exists as axial conformer in the low temperature as well as in the high pressure crystals, unlike all other mono-substituted cyclohexanes known.

The following observations were made:

(1). The shock frozen sample formed by slowly evaporating CCN on a window at 90 K was amorphous, had a glassy appearance and the conformational equilibrium of the vapour at 300 K was maintained.

(2). Gradual heating to *ca.* 150 K had no effect, but at 170 K the sample appeared frosty and the *e* bands were slightly enhanced relative to the *a* bands.

(3). When the sample was kept at 190 K for 1–2 h, the *e*-bands disappeared and the *a*-bands remained.

(4). At 215 K the *e*-bands returned, the sample looked glassy, and the *e/a* ratio was close to the value at 150 K. The spectrum remained unchanged until 260 K when the sample evaporated from the window.

(5). When the sample heated above 215 K was recooled to 190 K or lower and kept for two hours no spectral changes occurred.

The observations together with those made under pressure (see below) lead to the following conclusions: (a) CCN is present as a plastic (cubic, rotating) phase between melting and *ca.* 210 K with both conformers in equilibrium, (b) an anisotropic phase exists below *ca.* 210 K consisting of axial molecules, (c) conversion from the plastic to the anisotropic phase "does not occur" (is extremely slow), (d) conversion from the amorphous to the anisotropic phase is very slow, (e) a large similarity is observed between the spectra of the plastic and amorphous samples and (f) the shock frozen solid at 90 K maintains the conformational equilibrium of the vapour (300 K), but thermodynamic equilibrium is achieved at *ca.* 170 K.

High pressure solid. When CCN was compressed in the diamond anvil cell a solid phase was formed at *ca.* 1 kbar pressure. This solid appeared isotropic (plastic) in a polarization microscope, its IR spectrum (dashed curves in Fig. 2) was quite similar to the liquid spectrum (dashed-dotted curves) recorded at ambient pressure. A phase transition occurred fairly slowly at *ca.* 10–15 kbar between the plastic and an anisotropic phase. The spectrum

of the latter phase (solid curves in Fig. 2) was identical to our earlier¹⁰ results and contained the axial conformer only. Two or three single crystals dominated the sample and a distinct dichroic effect was observed with polarized radiation. The bands enhanced in one preferred direction are designated I_{\parallel} and those enhanced in a direction at right angle to the formed are labelled I_{\perp} in Table 1.

Spectral interpretation. No established correlations are known between the vibrational spectra and the conformations of hydrocarbons containing cyano and isocyano groups similar to the well known relationships for chloro-, bromo- and iodo-substituted hydrocarbons. The high pressure conformer was attributed as axial,¹⁰ based upon various criteria, including band intensity variations with temperature and spectral similarities. Later CCN-thiourea clathrates were made,²⁰ supporting the earlier conclusions. Moreover, the bands around 640 cm^{-1} assigned to the axial conformer (Tables 1 and 3) agree with the "spectral indicator" recently attributed²¹ to the *a* conformer. Finally, our present force constant calculations agree with this assignment.

With 19 atoms in the molecule and C_s symmetry, CCN should have 29 *a'* and 22 *a''* fundamentals for each conformer, of which many will coincide. The bands were assigned on the following criteria: (1) bands present in the low temperature or high pressure crystals should be axial or be common to the axial and equatorial conformers, (2) those present in the liquid and the plastic and amorphous solids, vanishing in the anisotropic crystals, should be equatorial, (3) the polarized Raman bands belong to species *a'*, the depolarized to *a''*; similar conclusions can be drawn from the dichroism of the axial bands in the high pressure crystal.

Force fields for CCN (and CNC) were transferred from *trans*-1,4-dihalocyclohexanes¹³ and the monohalocyclohexanes^{14,15} and extended with force constants for the side chain. Thus, 30 force constants were transferred and held fixed during the iterations, while 28 parameters for the following molecules, CCN, CNC, ethynylcyclohexane¹⁸ and *trans*-1,4-dicyanocyclohexane,¹⁶ were allowed to vary. The detailed force field and the procedure will be discussed elsewhere,¹⁸ whereas the calculated wave numbers for the *e* and *a* conformers are listed in Table 3. These data were of great help for the assignments and, as is apparent, the agreement between the observed and calculated wave numbers is quite satisfactory.

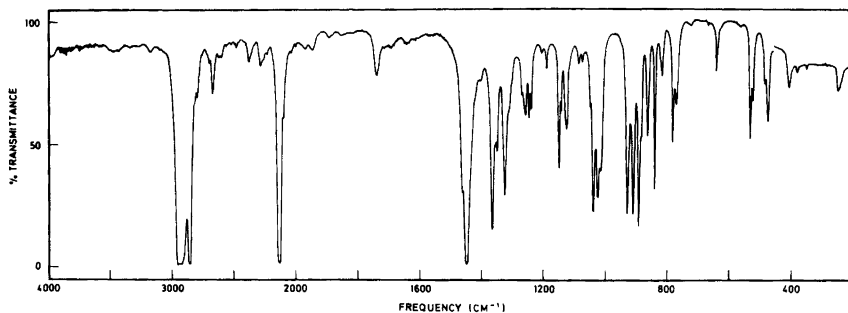


Fig. 4. The infrared spectrum of isocyanocyclohexane (CNC) as a liquid.

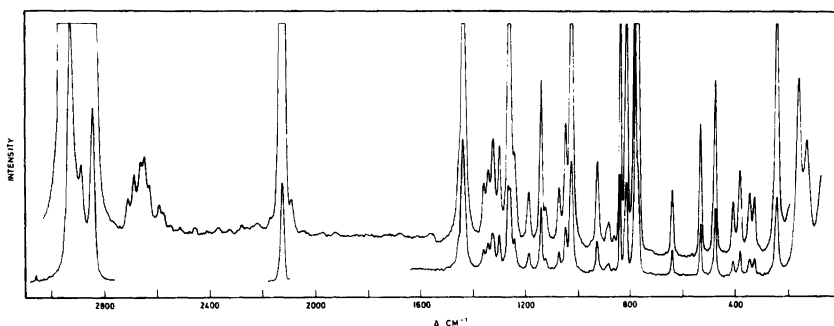


Fig. 5. Raman spectrum of isocyanocyclohexane (CNC) as a liquid.

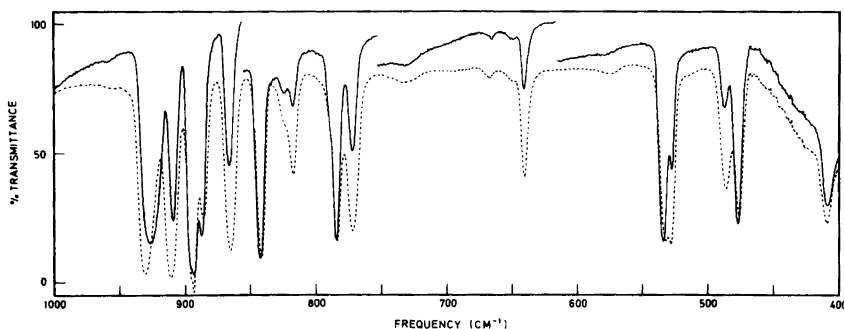


Fig. 6. Infrared spectra of isocyanocyclohexane (CNC) as an unannealed (dashed curve) and annealed solid (solid curve) at 90 K.

As immediately apparent from the columns in Table 3, CCN and CNC have nearly "identical" spectra. Apart from the $\text{C}\equiv\text{N}$ and $\text{N}\equiv\text{C}$ stretching vibrations (ν_8) observed at 2240 and 2140 cm^{-1} , respectively, the corresponding fundamentals in CCN and CNC are mostly a few cm^{-1} apart. Other exceptions are ν_{25} (*e*) as well as ν_{48} and ν_{49} including

both conformers of CCN and CNC, all of these involve bending modes of the side chain.

Isocyanocyclohexane (CNC)

Low temperature solid. CNC was studied in IR and Raman cryostats by the same procedure as

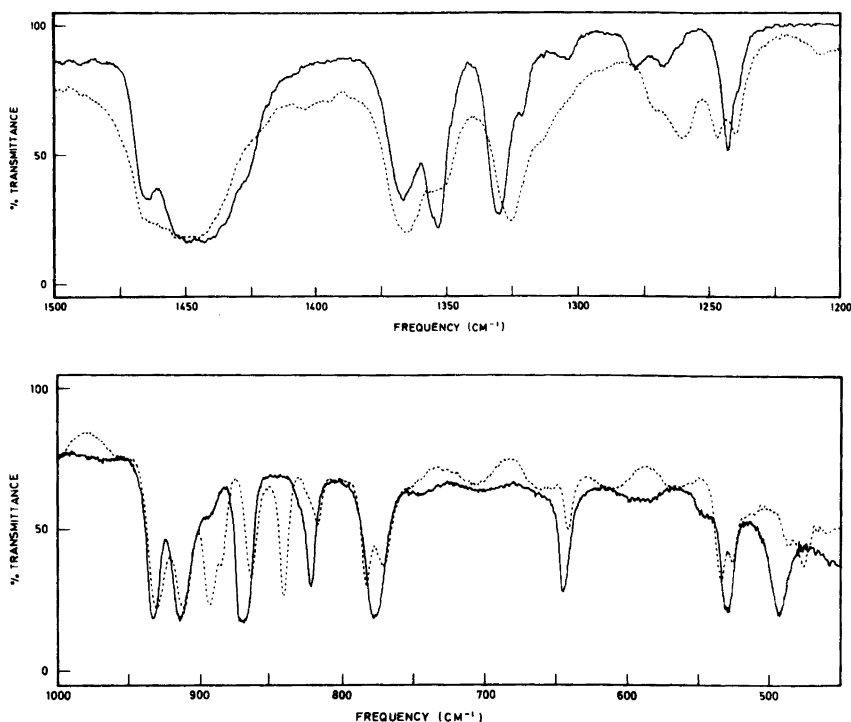


Fig. 7. Infrared spectra of isocyanocyclohexane (CNC) in the diamond anvil cell as a liquid at negligible pressure (dashed curve) and as an anisotropic crystal at ca. 20 kbar (solid curve).

described for CCN. In spite of many attempts with prolonged annealing at different temperatures, we were not able to "isolate" one conformer of CNC in the solid phase. Apparently, CNC is still more difficult to crystallize by cooling technique than CCN.

When the shock frozen amorphous solid was heated from 90 K to 170 K the e/a ratio increased as observed for CCN. Further heating to 210 K resulted in a small decrease in the e/a ratio in agreement with a small negative ΔH value between the conformers. None of the IR curves showed correlation splitting and the band width indicated that the sample was not crystalline in spite of a frosty appearance. At ca. 240 K the sample lost its frosty look and the e/a ratio increased considerably, in what presumably was a plastic phase. The solid tended to evaporate from the window and the sample was shock frozen to 90 K without any significant change in conformational equilibrium. The region 1000–400 cm^{-1} is shown in Fig. 6 giving the unannealed (dashed curve) and annealed (240 K) solid curve; both spectra were recorded at 90 K.

High pressure solid. When compressed, CNC behaved much like CCN, at ca. 2 kbar inspection in the polarization microscope suggested the formation of a plastic phase. The spectrum of this phase is not given in Fig. 7 but had slightly stronger a -bands than the liquid spectrum (dashed curve). At ca. 13 kbar a phase transition took place and an anisotropic crystal was formed in a matter of 10 min (the solid line of Fig. 7). A number of bands vanished in the high pressure crystal and the axial conformer remained as was the case for CCN. High pressure spectra were recorded in the whole spectral region and these data were essential for the spectral assignments.

Thiourea clathrate. CNC-thiourea clathrates were prepared as described²⁰ and the IR guest bands in the region 1000–800 cm^{-1} (representing a window between the host bands) were useful for conformational identification (compare Figs. 1 and 2 of Ref. 20). Distinct IR bands of the clathrate as a nujol mull were observed at 931, 912, 890, 864 and 841 cm^{-1} . The two former bands (931 and 912 cm^{-1}) are both attributed to overlapping e and a

Table 2. Infrared and Raman spectral data ^a for isocyanocyclohexane (CNC).

Liquid	Amorphous (90 K)		Annealed (238 K)		Crystalline		Assignments	
	Raman	IR 90 K	Raman 90 K	IR 90 K	IR (High pressure)	IR (High pressure)	equatorial	axial
2940 vs, bd	{ 2947 sP 2930 s,sh,D? 2909 s,P 2863 s,P	2940 vs, bd 2905 s 2860 vs, bd	2945 s	2950 vs 2920 vs 2898 s 2854 vs	2945 s	2960 vs	$\nu_1 a'$ $\nu_2, \nu_3, \nu_{30} a', a''$ $\nu_3, \nu_4, \nu_{31} a', a''$ $\nu_5, \nu_6 a'$ $\nu_{32}, \nu_{33} a''$ $\nu_7 a'$	$\nu_1 a'$ $\nu_2, \nu_{30} a', a''$ $\nu_3, \nu_4, \nu_{31} a', a''$ $\nu_5, \nu_6 a'$ $\nu_{32}, \nu_{33} a''$ $\nu_7 a'$
2185 vw	2848 w	2187 vw		2177 vw			comb.	$\nu_8 a'$
2137 vs, bd	2137 s,P	2145 vs, bd	2144 s	2142 vs, bd	2145 s		comb. A'	$\nu_9 a'$
2103 w	2103 m,P	2107 w	2105 w	2106 w	2105 w			$\nu_{10} a'$
1464 m	1465 m,P?	1465 m	1462 m	1465 m	1463 m	1464 m		$\nu_{34} a''$
1450 vs	1447 s,D?	1455 m,sh	1445 s	1450 s	1441 s	1445 vs, bd		$\nu_{35} a''$
		1447 vs		1445 s				$\nu_{11} a'$
1436 m,sh		1442 m,sh		1436 m				comb.
1420 vw	1437 w,sh	1436 m,sh		1423 w		1418 vw?		$\nu_{12} a'$
1404 w		1423 w		1408 w		1404 w		$\nu_{36} a''$
1368 s	1366 m,P	1367 s	1366 m	1366 s	1364 m	1364 s		$\nu_{13} a'$
1358 w		1354 m		1358 w		1356 m		$\nu_{14} a'$
1352 w	1350 m,D?		1347 m	1352 w } 1348 m }	1348 m	1349 w		$\nu_{15} a'$
				1339 w				$\nu_{37} a''$
1328 m	1334 m,P?	1327 s	1331 m	1334 w,sh		1325 s		$\nu_{13}, \nu_{38} a', a''$
1313 w	1327 w,sh,P			1328 m		1325 s		$\nu_{14} a'$
1305 vw	1306 m,D?	1305 w	1303 s	1317 w		1314 w		$\nu_{45} + \nu_{49} A'$
1272 w	1271 s,D	1272 m	1270 s	1304 w		1306 w		$\nu_{39} a''$
1265 w,sh	1266 s,P	1266 w,sh	1262 s	1271 w,sh		1270 w		$\nu_{40} a''$
1260 w	1260 w,sh,D	1261 m	1246 m	1264 w,sh		1260 m		$\nu_{15} a'$
1248 w	1248 m,D	1248 w		1260 m		1246 w		$\nu_{40} a''$
1241 w	1240 w,sh,P?	1239 m		1246 w		1246 w		$\nu_{16} a'$
1209 w		1211 w		1238 w		1239 m		$\nu_{16} a'$
1192 w	1193 m,D	1192 m	1192 m	1210 w		1210 w		$\nu_{29} + \nu_{42} = 1219 A''$
1169 vw?		1170 vw		1192 m		1192 w		$\nu_{41} a''$
1153 m	1153 w,sh,D?	1153 s		1170 vw		1153 s		comb.
				1152 m		1153 s		$\nu_{41} a''$

Table 2. Continued.

1146 w	1146 s,P	1147 m	1145 s	1147 m	1145 s	1146 m	*	$v_{17} a'$ comb.
1133 w,sh		1133 s		1142 vw,sh		1135 w,sh	1140 w,sh?	$v_{42} a''$
1128 m	1128 m,P	1128 s		1134 w		1127 s	1132 s	$v_{17} a'$
1116 vw		1116 w	1127 w	1128 m		1117 vw,sh		comb.
1097 vw?		1097 vw		1117 w				
1089 w	1090 vw?	1089 m		1089 m		1089 w	*	$v_{42} a''$
1077 w	1076 m,D	1077 m	1076 m	1077 m	1076 m	1078 w	1085 w	$v_{43} a''$
1052 m	1051 m,D	1052 m	1051 s	1051 m	1051 s	1051 m	*	$v_{44} a''$
1041 s		1041 s		1040 s		1041 s	*	$v_{18} a'$
		1033 m		1034 w,sh		1033 w	1033 s	$v_{18}, v_{44} a', a''$
1027 s	1029 s,D	1024 s	1029 s	1023 s	1028 s	1025 s	*	$v_{19} a'$
1017 m		1017 s		1016 m,sh		1017 s	1017 s	
951 vw	951 vw?	955 vw		959 vw				comb.
931 s	929 m,P	930 s	926 m	926 s	925 m	930 s	933 s	$v_{20} a'$
912 s	913 vw,D?	911 s	911 vw	909 m	891 m	911 s	914 s	$v_{45} a''$
893 s	893 w,D	893 vs	890 w	893 s	891 m	894 s	894 w	comb.
885 m	884 w,P	886 m		887 m		888 m,sh		
864 m	864 w,P	865 s	864 w	866 m	865 vw	866 s	870 s	$v_{21}, v_{46} a', a''$
841 s	841 s,P	841 s	842 s	842 s	843 s	843 s	*	
823 w,sh	823 w,sh,D?	824 w,sh	819 s	824 w	819 m	827 w,sh		
817 w	817 s,P	818 m	819 s	818 w	819 m	820 w	822 m	$v_{22} a'$
		790 w,sh		790 w,sh			*	comb.
783 m	783 s,P	784 s	783 s	784 s	785 s	785 s	*	$v_{47} a''$
770 m	774 s,sh,P		772 s	772 m	772 m,sh	774 m		$v_{23} a'$
642 w	642 m,P	641 m	640 m	641 w	640 w	644 w	647 m	$v_{23} a'$
536 m	535 s,P	534 s	532 m	536 s	535 m	538 m	*	$v_{47} a''$
528 m		530 s		529 m		529 m	531 s	$v_{24} a'$
488 w	488 w,sh	488 m	478 s	489 w	480 s	490 m	494 s	$v_{48} a''$
479 m	480 s,P	478 m	411 m	479 s	412 m	478 m	*	$v_{25} a'$
410 m	410 m,D	410 m	384 m	410 m	384 m	413 m	419 vw	$v_{25}, v_{48} a', a''$
384 w	384 m,P	384 w	353 w	382 w	351 m	385 w	402 w	$v_{49} a''$
351 w	349 m,P	352 w	331 m	352 w	332 w	352 w	352 w	$v_{26} a'$
	331 m,P	334 vw	247 m	331 m	247 m	352 w	339 w	$2 \times v_{51} A'$
250 m		254 w		254 w			254 w,sh	$v_{27} a'$
	243 s,D	246 m	162 m	246 m	166 m		246 m	$2 \times v_{51} A'$
170 m	160 s,D		132 m		135 m		188 m	$v_{28}, v_{50} a', a''$
150 m	130 m,D						181 m	$v_{51} a''$
							140 m	$v_{29} a'$

*See footnote to Table 1.

Table 3. Observed^a and calculated fundamental frequencies for cyano- and isocyanocyclohexane.

	Cyanocyclohexane				Isocyanocyclohexane			
	<i>e</i>		<i>a</i>		<i>e</i>		<i>a</i>	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
<i>a'</i>								
<i>v</i> ₁	2955	2957	2945	2958	2947	2957	2947	2958
<i>v</i> ₂	2933	2922	2933	2922	2930	2922	2930	2922
<i>v</i> ₃	2927	2916	2914	2916	2930	2916	2909	2916
<i>v</i> ₄	2901	2914	2901	2914	2909	2914	2909	2914
<i>v</i> ₅	2860	2857	2860	2857	2860	2857	2863	2857
<i>v</i> ₆	2860	2853	2860	2854	2860	2853	2863	2854
<i>v</i> ₇	2860	2851	2860	2851	2860	2851	2848	2851
<i>v</i> ₈	2240	2240	2240	2240	2137	2140	2137	2140
<i>v</i> ₉	1465	1456	1465	1456	1464	1456	1464	1456
<i>v</i> ₁₀	1452	1439	1447	1437	1450	1440	1442	1437
<i>v</i> ₁₁	1437	1427	1426	1422	1420	1427	1420	1422
<i>v</i> ₁₂	1405	1390	1364	1366	1404	1399	1366	1381
<i>v</i> ₁₃	1341	1343	1353	1346	1339	1343	1350	1346
<i>v</i> ₁₄	1318	1303	1318	1337	1334	1311	1327	1340
<i>v</i> ₁₅	1270	1253	1264	1263	1265	1253	1265	1264
<i>v</i> ₁₆	1239	1232	1231	1231	1248	1233	1241	1233
<i>v</i> ₁₇	1136	1134	1123	1133	1146	1135	1128	1137
<i>v</i> ₁₈	1041	1032	1031	1031	1041	1041	1033	1031
<i>v</i> ₁₉	1031	1023	1014	1005	1027	1023	1017	1005
<i>v</i> ₂₀	931	922	935	927	931	928	931	933
<i>v</i> ₂₁	882	891	862	857	885	891	864	856
<i>v</i> ₂₂	839	934	817	814	841	834	817	815
<i>v</i> ₂₃	779	763	771	776	783	765	774	779
<i>v</i> ₂₄	540	535	638	643	536	530	642	640
<i>v</i> ₂₅	506	505	496	493	479	482	488	490
<i>v</i> ₂₆	385	401	392	391	384	397	384	388
<i>v</i> ₂₇	359	363	371	367	351	351	331	321
<i>v</i> ₂₈	267	283	257	275	243	251	250	254
<i>v</i> ₂₉	124	136	124	110	130	129	130	107
<i>a''</i>								
<i>v</i> ₃₀	2927	2918	2927	2917	2930	2918	2930	2918
<i>v</i> ₃₁	2914	2913	2914	2913	2909	2913	2909	2913
<i>v</i> ₃₂	2860	2855	2860	2855	2860	2855	2863	2855
<i>v</i> ₃₃	2860	2852	2860	2852	2860	2852	2863	2852
<i>v</i> ₃₄	1447	1441	1447	1440	1445	1441	1447	1440
<i>v</i> ₃₅	1440	1432	1437	1433	1436	1432	1436	1433
<i>v</i> ₃₆	1364	1377	1364	1368	1368	1377	1368	1368
<i>v</i> ₃₇	1353	1347	1354	1350	1350	1347	1358	1350
<i>v</i> ₃₈	1327	1344	1350	1340	1328	1344	1350	1340
<i>v</i> ₃₉	1298	1300	1318	1298	1305	1300	1306	1298
<i>v</i> ₄₀	1258	1244	1281	1255	1260	1244	1272	1255
<i>v</i> ₄₁	1185	1188	1143	1156	1192	1188	1153	1156
<i>v</i> ₄₂	1094	1095	1123	1136	1089	1094	1133	1136
<i>v</i> ₄₃	1076	1071	1083	1078	1077	1071	1077	1078
<i>v</i> ₄₄	1048	1052	1031	1035	1052	1053	1033	1035
<i>v</i> ₄₅	921	910	921	933	912	911	912	933
<i>v</i> ₄₆	892	889	862	857	893	889	864	856
<i>v</i> ₄₇	788	788	788	788	790	788	771	788
<i>v</i> ₄₈	505	494	547	542	479	460	528	512
<i>v</i> ₄₉	431	459	421	437	410	430	410	417
<i>v</i> ₅₀	238	228	267	256	243	227	243	234
<i>v</i> ₅₁	162	169	162	147	160	149	160	137

^aWhenever appropriate wave numbers from the infrared and Raman liquid spectra are given.

bands and therefore give no conformational clue. The 864 cm^{-1} line, assigned as an axial band, was the most intense of the remaining bands whereas 841 cm^{-1} (e band) was hardly visible and 890 cm^{-1} (consisting of overlapping e bands at 893 and 885 cm^{-1}) was weak. Compared with the intensities of these bands in the liquid (Fig. 4) the e/a ratio is probably a factor of 10 lower in the clathrate than in the liquid. Thus, the a conformer is highly preferred for the CCN and the CNC as well as the chloro- and bromocyclohexane clathrates.²⁰ For iodocyclohexane²⁰ the a conformer is less preferred and for fluorocyclohexane¹⁴ the clathrate consists of guest molecules in nearly the same conformer mixture as in the liquid.

Spectral interpretations. The IR and Raman bands of CNC were attributed to equatorial and axial conformers using the same criteria as for CCN (although less conclusive for CNC since the isolated a -conformer was not obtained in the low temperature IR and Raman spectra). A striking similarity to the CCN spectra was of particular help and the results of the force constant calculations were essential for the spectral interpretations.

DISCUSSION

CCN is to our knowledge the only monosubstituted cyclohexane which is shown to crystallize in the axial conformer at low temperatures. Obviously the conformer adopted by the molecules in the crystal depends upon the ΔG° between the conformers at the temperature of crystallization as well as specific interactions in the crystal lattice which may favour one or the other conformer. The low ΔG° for CCN and CNC at the coalescence temperatures (183 – 193 K) means nearly equal concentration of the conformers (although the equatorial is slightly more abundant). Therefore, the crystal interactions will be the deciding factor and apparently favour the axial conformer for CCN.

For crystallizations at higher pressure the conformational equilibrium will be further influenced by the volume difference between the conformer molecules; the smaller volume conformer will be favoured under pressure. It was shown²² for chloro- and for *trans*-1,4-dihalocyclohexanes in CS_2 solution that the $a(aa)$ conformer had a partial molar volume ($\Delta\bar{V}$) which was 1.9 – $3.8\text{ cm}^3/\text{mol}$ smaller than $e(ee)$ for these compounds. At least for monohalo-, *trans*-1,2-

dihalo- and *trans*-1,4-dihalocyclohexanes, the more spherical, axial (diaxial) conformer always appears to have smaller volume than the more ellipsoidal equatorial (diequatorial) conformer.²³ The *trans*-1,4-dihalocyclohexanes (involving chlorine, bromine and iodine) are converted from an “ ee -crystal” to an “ aa -crystal” under 30 – 50 kbar pressure.^{11–13} Moreover, *trans*-1,2-bromochlorocyclohexane²⁴ and isocyanatocyclohexane¹⁰ crystallize in the $ee(e)$ conformer at low temperature and in the aa (a) conformer at high pressure, again revealing the preference for the axial conformers under pressure. With this background, the high pressure crystallization of CCN and CNC in the axial form is not surprising.

Large difficulties were encountered in the low temperature crystallization of CCN while for CNC the attempts were not successful. Apparently, the existence of plastic phases in CCN and CNC, common to cyclohexanes with small substituents,²⁵ made conversion to the anisotropic phase quite difficult.

Similar difficulties were found for fluorocyclohexane¹⁴ also containing a plastic phase, which earlier workers²⁶ had not been able to crystallize. However, in fluorocyclohexane a reversible transition between the plastic and the anisotropic crystals was obtained by temperature variation, which was not obtained for CCN and CNC. With still more sophisticated cooling and annealing technique an anisotropic crystal of CNC might be grown. In the high pressure diamond anvil cell, however, the various phase transitions took place readily, emphasizing the importance of this technique.

The anomalous stabilization of the diaxial form of *trans*-1,4-dihalocyclohexane compared with the monohalocyclohexane was interpreted²⁷ as due to 1,3-attractions between the negative halogens and the hydrogens which were calculated to be more positive than usual for these molecules. In *trans*-1,4-dicyanocyclohexane no corresponding stabilization of the diaxial conformer compared with CCN was observed.¹⁶ However, no corresponding electrostatic attraction seems favourable for this molecule.

The cyano and isocyano groups with cylindrical symmetry are found to have low conformational preferences,¹ and their effective van der Waals radii are affected by the electron densities in their outer orbitals.⁶ The isoelectronic ethynyl ($\text{C}\equiv\text{C}-\text{H}$) cyclohexane has a higher preference¹ for the

equatorial conformer than CCN and CNC (it also crystallizes in the equatorial conformer at low temperature and at high pressure¹⁸). This difference from CCN was correlated with a high electronic density at the carbon bonded to the ring in ethynylcyclohexane,⁶ lowered in CCN due to the electronegative N atom with its lone pair orbital.

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