

## Conformational Spectroscopic Studies of Cyano- and Isocyanatocyclohexane

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The IR spectra of cyano- and isocyanatocyclohexane as liquids, in solution and as solids at  $-175^{\circ}\text{C}$  were recorded in the region  $4000-200\text{ cm}^{-1}$ . Spectra of the high pressure crystals were obtained with the aid of a high pressure cell having diamond windows. Raman spectra of the compounds as liquids and low temperature solids were recorded.

Both compounds form a mixture of *e*- and *a*-conformers in the liquid state and in solution. At low temperature isocyanatocyclohexane crystallizes in the *e*-conformer whereas both conformers were present in solid cyanocyclohexane probably as a result of incomplete crystallization. When pressurized to *ca.* 20 kbar at ambient temperature both compounds crystallize in the *a*-conformation as observed for certain dihalocyclohexanes. The vibrational spectra have been discussed and compared with those of other monosubstituted cyclohexanes.

We have for a long time been interested in the vibrational spectra of halogenated cyclohexanes and various monohalo- and *trans*-1,2-dihalo-cyclohexanes have been investigated. The purpose of this work was to study the conformational equilibria in the liquid state (and possibly in the vapour) and particularly to decide which conformer was present in the crystal. For this purpose we have successfully utilized high pressure crystallization at ambient temperature in addition to low temperature crystallization under atmospheric pressure. The low temperature and the high pressure crystals most often consist of molecules in the same conformation. However, when the enthalpy difference between the conformers is small, intermolecular crystal forces may become the deciding factors and the low temperature and the high pressure crystals

can have molecules in different conformations.<sup>1,2</sup> These cases are intrinsically interesting, and besides, they offer excellent opportunities for interpreting the vibrational spectra in detail and assigning the bands to one or the other conformers.

The studies have now been extended to other substituted cyclohexanes, and in the present communication we will present our results for cyanocyclohexane ( $\text{C}_6\text{H}_{11}\text{CN}$ ) and isocyanatocyclohexane ( $\text{C}_6\text{H}_{11}\text{NCO}$ ), later called CCN and CNCO, respectively. The conformational equilibria for CCN and CNCO in solution have previously been investigated by NMR technique,<sup>3,4</sup> further by equilibration measurements<sup>5,6</sup> of the *cis* and *trans* isomers of 4-*t*-butylcyclohexylcyanide. To our knowledge, no vibrational spectral studies of these compounds have been reported, nor have they ever been investigated as pure liquids or in the crystalline state.

### EXPERIMENTAL

The samples of CCN and CNCO were commercial products from the K & K laboratories and from Koch-Light, respectively. They were fractionated three times under reduced pressure. When checked by gas chromatography CCN was found to be better than 99.5% pure, whereas CNCO had *ca.* 11% impurities. Therefore, CNCO was treated by preparative gas chromatography, after which 10 IR bands present in the impure sample disappeared.

The IR and Raman spectrometers and the high pressure diamond cell<sup>7</sup> have been described.<sup>8</sup> The low temperature Raman spectra were obtained by  $90^{\circ}$  illumination technique using a cryostat<sup>9</sup> with a cold copper tip.

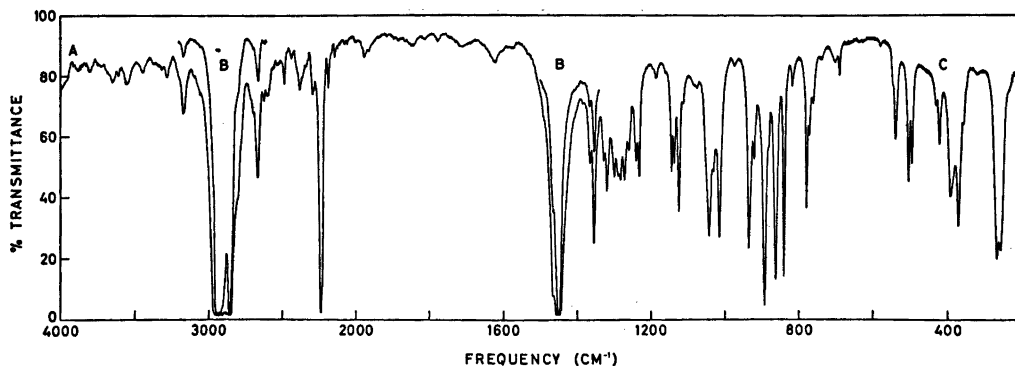


Fig. 1. The IR spectrum of liquid cyanocyclohexane. A, 0.1 mm KBr cell; B, 0.025 mm KBr cell, and C, 0.2 mm polyethylene cell.

## RESULTS AND DISCUSSION

### Cyanocyclohexane

The IR spectra of CCN in the liquid state and as high pressure crystal are shown in Figs. 1 and 2, respectively, while the IR and Raman frequencies are listed in Table I. With 19 atoms, CCN should have 51 fundamental frequencies for each conformer out of which *ca.* 35 should appear below 1400  $\text{cm}^{-1}$ . Since *ca.* 45 strong or medium intense IR or Raman bands were observed in this region an estimated 25 bands may be attributed to overlapping fundamentals for both conformers with *ca.* 20 vibrational modes appearing as distinct bands for each conformer.

*Low temperature solid.* As apparent from Table I no significant simplification of the IR or Raman spectra were observed upon cooling to a solid in contradiction to the results previously obtained for mono<sup>10,11</sup> and dihalogenated<sup>1,8,12-14</sup> cyclohexanes. Several attempts were made to anneal the sample just below the melting point before cooling down to  $-175^\circ\text{C}$ , but no apparent changes were observed in the spectra. It is well known that certain cyclohexanes, *e.g.* fluoro- and chlorocyclohexane as well as *trans*-1,4-dichlorocyclohexane,<sup>15</sup> solidify into a disordered, rotating phase consisting of both conformers before reaching a transition temperature and converting into an anisotropic

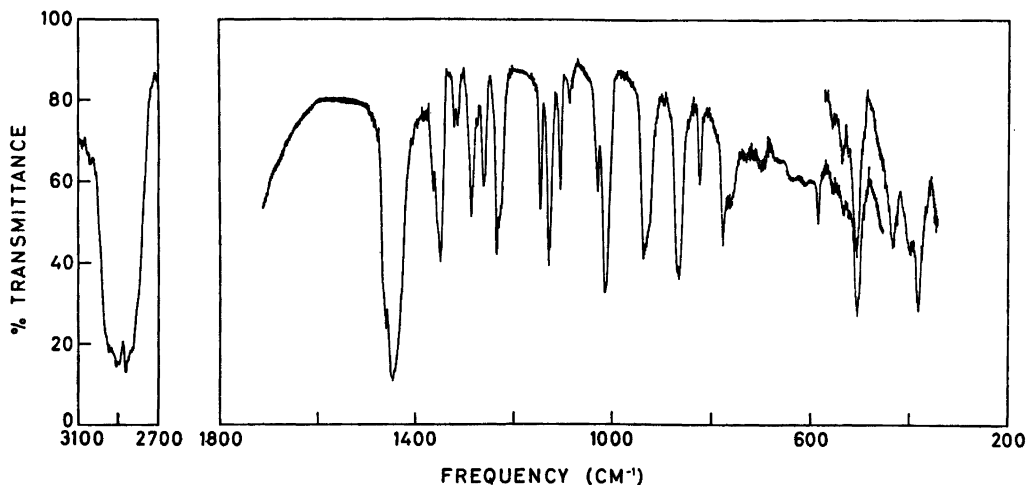


Fig. 2. The IR spectrum of polycrystalline cyanocyclohexane at ambient temperature (*ca.* 20 kbar pressure).

Table 1. Infrared <sup>a</sup> and Raman spectral data of cyanocyclohexane.

Liquid		Solid IR		Raman		Conformer <sup>b</sup>
IR	Raman	Low temp. (-175 °C)	High press. (~20 kbar)	Low temp. (-175 °C)		
3171 w <sup>e</sup>		3170 w	3170 w			
2948 s, sd	2947 vs	2950 s, sd		2948 s		
2928 vs	2928 s, sd	2929 vs		2930 m		
			2900 vs, bd			
2903 s, sd	2904 s	2904 s, sd		2902 m		
2859 vs	2861 vs	2860 vs		2860 s		
2800 w, sd		2801 w, sd				
2663 m		2665 m	2668 m			
2291 vw		2290 vw				
2240 vs	2241 vs	2240 s		2240 s		a, e
2235 s, sd	2236 m, sd	2234 m, sd		2236 m, sd		
2183 vw	2184 vw	2182 vw				
1490 vw, sd						
1465 s, sd	1464 m, sd P	1465 m	1465 s, sd			a, e
1450 vs, bd	1448 vs D	1450 vs	1450 vs, bd	1448 s		a, e
1364 m, sd	1364 m P	1362 w	1363 w, sd			a, e
		1353 m				
1352 s	1354 m D		1352 vs	1360 w, bd		a, e
		1349 m				
1326 m	1328 m	1328 w, sd	1325 m	1327 w		a
1317 m	1319 w, sd	1320 m	1316 m	1320 vw		a, e
1297 m	1298 s D	1298 m	* <sup>d</sup>	1298 s		e
1286 w, sd		*				a
			1286 s			
1281 m		1281 m				a, e
1270 m	1272 vs D	1270 m	*	1271 s		e
1258 m	1260 s D	1260 m	1261 s	1260 s		a, e
1239 m	1239 m P	1239 m	1239 vs	1239 w		a, e
1231 m	1232 w, sd	1230 m	1230 m			a
1185 w	1186 m D	1185 w	*	1186 w		e
1143 m	1143 w, sd	*	1144 s			a
1136 m	1137 s P	1136 m	*	1138 m		e
1123 s	1124 m D	1126 m	1128 s			a
1112 w	1112 vw	1110 w	1110 m			a, e
1082 vw	1082 w, sd	1085 w, bd	1086 w			a, e
1074 vw	1075 m D	1074 vw	*	1077 w		e
1042 s	1044 s P	1043 s	*	1045 s		e
1031 w, sd	1032 vs D	1033 m	1031 m, sd	1033 vs		a, e
1013 s		1015 m	1015 vs			a
		937 w				
935 s	933 s P		937 s, bd	932 m		a, e
		930 m				
920 m	920 w	922 vw	925 w, sd			a, e
892 s	893 w D	894 vs	*	891 w		e
882 w, sd	881 m D	882 w	*	884 m		e
862 s	862 w	865 s	867 s			a
840 s	840 s P	842 s	*	843 m		e
817 w	817 s P	829 w	820 m	821 m		a
779 s	779 vs P	780 s	778 s	780 vs		a, e
771 m, sd	772 s D	773 w, sd				a, e
762 w, sd		760 w, sd	758 w, sd			a, e
739 vw		745 vw				
701 vw		702 vw	707 vw			
689 w		689 w	*			e
580 vw		582 vw	582 m			a, e
547 w, sd		547 w, sd	549 w			a, e

Table 1. Continued.

540 m	541 s P	540 m	*	543 s	<i>e</i>
505 m	506 m P	509 s	*	508 w	<i>e</i>
496 m	496 m	499 w	501 s		<i>a</i>
431 w	431 m D	431 w	*	430 m	<i>e</i>
422 m	422 w, sd	421 w	430 m		<i>a</i>
391 m	391 w, sd D	392 w, sd	397 m, sd	390 vw	<i>a</i>
386 w, sd	387 w	388 m	*		<i>e</i>
371 s	372 m D	375 m	378 s		<i>a, e</i>
359 w, sd	359 m P	360 w		362 m	<i>a, e</i>
267 s	268 s D	272 vs		270 w	<i>e</i>
258 s	260 s P	258 vw, sd			<i>a</i>
	160 s D			162 w	<i>a, e</i>
	125 m P			132 w	<i>a, e</i>

<sup>a</sup> Very weak IR bands in the regions 4000–3200, 2600–2300 and 2200–1500 cm<sup>-1</sup> were omitted. <sup>b</sup> *a*, axial and *e*, equatorial. <sup>c</sup> Abbreviations: s, strong; m, medium; w, weak; v, very; sd, shoulder, bd, broad; P, polarized and D, depolarized. <sup>d</sup> Bands with an asterisk are absent in the solid state.

crystalline solid. However, differential thermal analysis (DTA) of CCN gave only one discontinuity in the temperature range –100 to 25 °C corresponding to the melting point. Thus, it seems likely that in spite of the annealing our low temperature sample was merely a glass as indicated by the lack of correlation field splitting in the IR and Raman spectra.

*High pressure solid.* In contrast to the low temperature, the high pressure IR spectrum was highly simplified compared to that of the liquid (Figs. 1 and 2). Evidently, only one conformer was present in the high pressure crystal, and various criteria were employed to decide if this conformer was the *e* or the *a*. IR spectra of liquid CCN were recorded at elevated temperatures (*ca.* 150 °C) and at low temperature (–10 °C) and compared with those at ambient

temperature (30 °C). Significant intensity variations of certain bands were observed with temperature. Measurements of band areas or absorbance values revealed that the bands present in the high pressure spectrum were enhanced at higher temperatures compared to those vanishing in the high pressure spectrum.

The following pairs of bands were investigated: 1136/1231, 1136/1123, 1136/1143, 1042/1013, 892/862, 840/862, 840/817, 505/496, 540/496, 432/422, and 267/258 cm<sup>-1</sup>. The thermodynamic functions ( $\Delta G$ ) for the  $e \rightleftharpoons a$  conversion reveal a preference of the equatorial conformer for nearly all monosubstituted cyclohexanes. The enthalpy terms ( $\Delta H$ ) are known for fewer systems, but when investigated,<sup>18</sup> the equatorial conformers appear the more stable. Applied to CCN, a negative  $\Delta H_{e-a}$  would therefore lead to

Table 2. Some characteristic vibrations in monosubstituted cyclohexanes in the region around 850 cm<sup>-1</sup>.

Conf.	CN	NC <sup>a</sup>	NCO	Cl <sup>b</sup>	Br <sup>b</sup>	I <sup>b</sup>
<i>e, a</i>	920 m	913 s	905 s	921 w	919 w	915 w
<i>e</i>	892 s	895 s	893 s	889 vs	885 vs	883 s
<i>e</i>	882 w	887 w	881 s	858 s	852 s	848 m
<i>a</i>	862 s	865 m	863 m	868 s	864 m	862 m
				852 m		
<i>e</i>	840 s	843 m	839 s	817 vs	810 vs	806 s
<i>a</i>	817 w	817 w	815 m	807 m	804 m	

<sup>a</sup> Data from Ref. 17, no conformations known. DMS card No. 6357. <sup>b</sup> Data from Ref. 11, distinction between *e* and *e+a* uncertain.

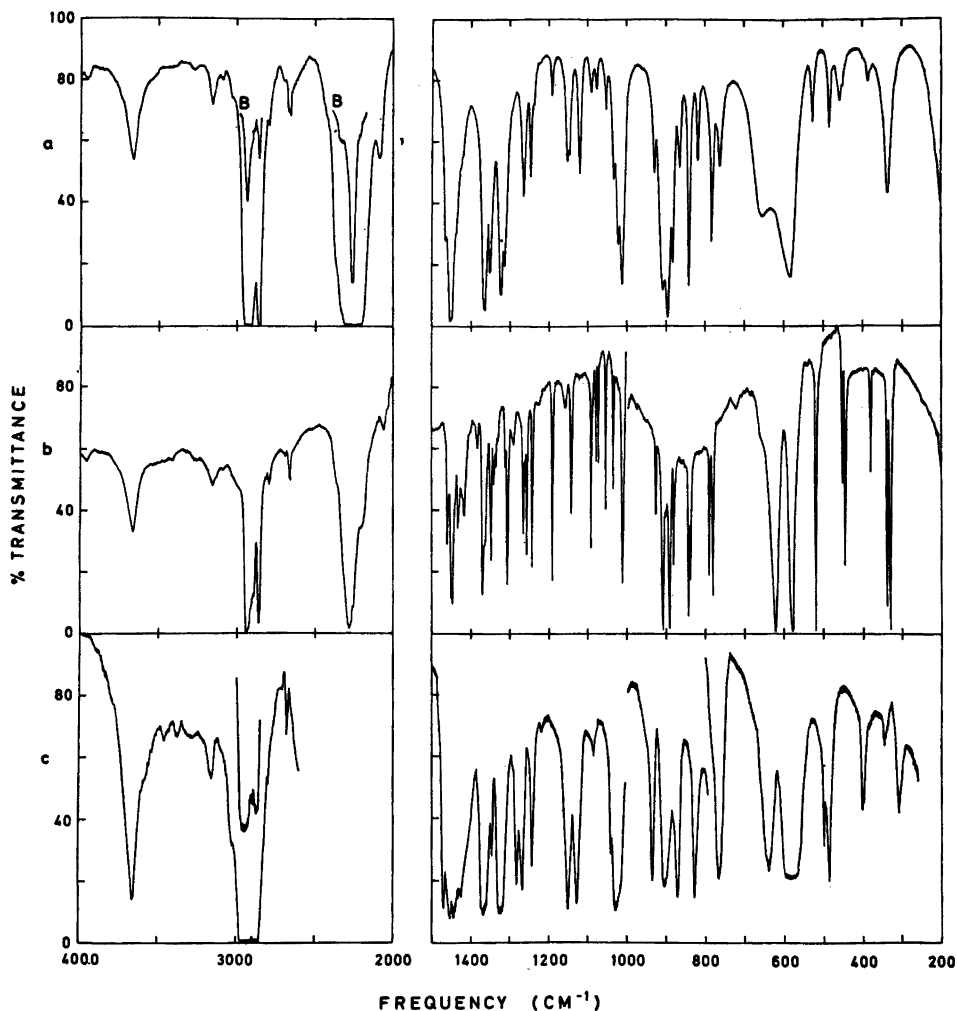


Fig. 3. The IR spectra of isocyanatocyclohexane: a. (upper curve) A, 0.05 mm. CsI cell and B, ca. 25 %  $\text{CCl}_4$  solution in 0.025 mm. KBr cell; b. (middle curve) polycrystalline solid at  $-175^\circ\text{C}$ , and c. (lower curve) polycrystalline solid at ambient temperature (ca. 20 kbar pressure).

the high pressure conformer being *a*. However, when extrapolated from the 4-*t*-butylcyclohexylcyanide, a  $\Delta H$  close to zero ( $\Delta H = 0.042 \pm 0.095$  kcal/mol) was suggested<sup>6</sup> for CCN, whereas calculations<sup>5</sup> based upon the van der Waals repulsions indicate that the *a*-conformer should be 0.46 kcal/mol less stable than the *e*-conformer.

Since the *e*- and *a*-conformers of CCN should have nearly the same dipole moment, no displacement of the conformational equilibrium with solvent polarity would be expected (and

none was found). A close comparison between the IR and Raman spectra of CCN with other related cyclohexanes might give a clue to the spectral attributions. The C—C stretching region around  $1000\text{ cm}^{-1}$ , found to be of diagnostic value<sup>8</sup> for the halogenated cyclohexanes (and for CNCO, see later) did not fall into this regular pattern, probably because of the additional exocyclic C—(CN) stretching mode falling into the same region for CCN. However, a remarkable similarity between the vibrational spectra of CCN, CNCO, and cyclohexylisocya-

Table 3. Infrared<sup>a</sup> and Raman spectral data for isocyanatocyclohexane.

Liquid IR	Raman	Solid IR		Raman Low temp. (-175 °C)	Conformer <sup>b</sup>
		High press. (~20 kbar)	Low temp. (-175 °C)		
3665 m <sup>c</sup>		3660 m	3642 w		
3160 w		3160 w	3160 vw		
2934 vs, bd	2943 vs	2940 vs, bd	2933 vs	2954 m, sd 2944 vs 2935 m, sd	
2913 m, sd	2900 m		2913 s	2902 m 2894 m 2861 vs	
2857 vs	2858 vs	2862 vs, bd	2852 s } 2799 w	2854 m, sd }	
2795 w			2669 w		
2670 w	2672 vw, sd	2671 w	2663 w	2670 vw, sd	
2660 w	2663 vw	2660 vw	2350 w, sd	2663 vw	
2350 m, sd			2282 vs, bd		
2255 vs, bd	2254 vw		2259 s, sd		
2210 s			2208 m, sd		
2090 m			2090 m		
1465 m, sd	1465 w, sd	1469 s	1461 m	1466 vw	
1453 vs		1452 s	1451 s, sd	1450 vs	
1449 vs			1448 s		
1437 m, sd	1443 vs	1442 s	1433 m	1443 vs	
1420 w, sd	1425 m, sd	1424 s	1417 m	1419 s	
			1383 w		
			1369 s		
1363 s	1365 w, sd	1370 s, sd } 1361 s }	1363 w, sd }	1369 w	a, e
1349 s	1348 m	1349 m	1348 s	1347 s, bd	a, e
			1341 w		
			1336 w		
1321 s	1322 w	1323 s, bd	* <sup>d</sup>	*	a
1311 s	1308 m	*	1312 w } 1307 s }	1308 s	e
			1291 w, bd		
1267 m, sd	1265 s	1282 s	1265 m	1267 vs	a, e
1262 s		1267 s	1257 s	1257 w	a, e
1245 s	1245 m	1243 s	1243 s	1244 m	a, e
1236 w, sd	1236 w, sd		*	*	a
1190 w	1190 w	*	1191 s	1193 m	e
1151 s		1150 s	*	*	a
1145 s	1145 m		1143 m	1145 s	a, e
1120 s	1120 vw	1127 s	*	*	a
1090 w		*	1091 m		e
1076 w	1076 w	1083 w	1078 m } 1073 m }	1077 s	a, e
1052 w	1052 m	*	1054 m	1054 m	e
1032 m	1030 s	1040 m	1035 m } 1029 vw }	1030 vs	a, e
1020 s		1028 s, bd	*		
1010 s	1012	*	1011 s	1012 s	e
928 m	926 vw	935 s	928 m	926 vw	a, e
905 s		905 s, bd	909 s	912 vw	a, e

Table 3. Continued.

893 s	893 w	*	893 s	894 vw	e
881 s	880 w	*	881 s	882 w	e
863 m		870 s	*		a
			843 s		
839 s	838 s	*	839 s	843 s	e
815 m	815 s	827 s,sh	*	*	a
780 s	780 vs	*	790 s	781 vs	e
			780 s		
759 m	761 s	767 s	*	*	a
650 s,bd	652 vw	641 vs	621 vs	644 w	a, e
598 m,sd	597 w		*	*	a
		580 s,bd			
580 s,bd	579 w,sd		579 vs	579 m	a, e
523 m	524 m	*	520 vs	523 m	e
		497 m,sd			
482 m	482 w	484 s	*	*	a
	459 m	*	453 m	456 s	e
455 w,bd					
	450 w,sd	*	445 s	448 m,sd	e
382 w	382 w	397 m	381 m	380 m	a, e
335 s	337 m	340 w	340 s	335 vs	a, e
			331 sv		
		308 m			
	175 w			175 w	a, e
				132 w	a, e

<sup>a</sup>Very weak IR bands in the regions 4000–3000 and 2000–1500  $\text{cm}^{-1}$  were omitted. <sup>b</sup>a, axial and e equatorial. <sup>c</sup>Abbreviations, see footnotes to Table 1. <sup>d</sup>Bands with an asterisk are absent in the solid state.

nide<sup>17</sup> was observed in the region 900–800  $\text{cm}^{-1}$ . As apparent from Table 2, the corresponding frequencies between CCN and CNCO fall within 2  $\text{cm}^{-1}$  and the band intensities show corresponding similarities. With the CNCO bands attributed to the e or a conformers (see below) the CCN bands were assigned correspondingly. Preliminary measurements indicate that also cyclohexylisocyanide bands follow the same pattern. Thus, the spectral relations also support the high pressure crystal to be in the a-conformer and the observed bands of Table 1 have been attributed accordingly. Only the e-bands can be attributed with certainty whereas the bands present in the high pressure solid can be a-bands or they are common to both conformers.

The IR band at 2240  $\text{cm}^{-1}$  was assigned as the  $\text{C}\equiv\text{N}$  stretching modes for both conformers since this frequency always seems independent of conformational changes. A weaker satellite at 2235  $\text{cm}^{-1}$  corresponds with the isotopic shift of the  $^{13}\text{C}\equiv^{14}\text{N}$  stretch.

### Isocyanatocyclohexane

The IR spectra of CNCO in the liquid, low temperature solid and high pressure solid are shown together in Fig. 3, whereas the IR and Raman frequencies are listed in Table 3. Having an additional atom, CNCO should have one more fundamental below 1400  $\text{cm}^{-1}$  than CCN. Because the CNC angles in isocyanates and isothiocyanates are different from 180°, rotational conformers might exist,<sup>18,19</sup> although no conformations were detected in alkylisocyanate.<sup>18</sup> The very low barrier to internal rotation around the C–N bonds, equal to  $83 \pm 15$  cal/mol in methylisocyanate<sup>20</sup> should indicate free or nearly free rotation, as recently discussed<sup>21</sup> for allylisocyanate and allylisothiocyanate. Although rotational conformers in CNCO cannot be completely ruled out, our data can be best interpreted in terms of a conformational equilibrium, derived from the cyclohexane ring conversion only.

*Low temperature solid.* When CNCO was cooled

Table 4. Some characteristic skeletal vibrations in monosubstituted cyclohexanes around 1000  $\text{cm}^{-1}$ .

Substituent	Axial IR	Raman	Equatorial IR	Raman
Cl <sup>a</sup>	1029 m	1028 vs	1029 m	1028 vs
	1014 s	1013 w	993 vs	993 s
Br <sup>a</sup>	1028 w	1028 s	1028 w	1028 s
	1010 m	1010 w	988 s	989 s
I <sup>a</sup>	1021 w	1023 s	1030 m	1032 s
	1006 s	1008 vw	988 s	988s
NCO	1032 m	1030 s	1032 m	1030 s
	1020 s		1010 s	1012 m

<sup>a</sup> Data from Ref. 8.

below the freezing point several IR or Raman bands diminished in intensity and disappeared completely after annealing (Fig. 3). The number of IR or Raman bands in the low temperature crystal agree with one conformer.

In order to decide if the low temperature solid had crystallized as *e*- or *a*-conformers, spectra were recorded of liquid CNCO at 150, 30 and  $-20^\circ\text{C}$ . Significant intensity variations were observed, interpreted as a shift in the conformational equilibrium. The following pairs of bands were suitable for measurements: 1010/1020, 893/863, 881/863, 839/815, and 780/759  $\text{cm}^{-1}$ , and in each case these intensity ratios became smaller at higher temperatures. Since the IR bands in the nominators were present and those of the denominations absent in the solid spectra, the low temperature crystal should therefore consist of molecules in the more stable conformer. As discussed previously, the *e*-conformation generally has the lower  $\Delta H$  value for monosubstituted cyclohexanes. For CNCO, NMR measurements<sup>4</sup> at 35 and at  $-75^\circ\text{C}$  clearly demonstrated a negative enthalpy difference ( $\Delta H$ ) and the low temperature crystal will therefore consist of molecules in the *e*-conformer in agreement with the halocyclohexanes.<sup>11</sup>

Our attributions of the bands present in the low temperature crystal as *e* were further supported by the spectral features of the ring stretching region around 1000  $\text{cm}^{-1}$ . The IR and Raman bands in this region are listed in Table 4 together with those of chloro-, bromo-, and iodocyclohexane.<sup>11</sup> It can be seen that the CNCO bands correspond particularly with those of the chloro- and bromocyclohexanes. The high

frequency band is attributed to both conformers in CNCO as well as in the chloro- and bromo-compound, but not for iodocyclohexane<sup>11</sup> or the dihalocyclohexanes.<sup>8</sup> The *e*-bands are invariably situated at lower frequencies and for several halo-<sup>11</sup> and dihalocyclohexanes<sup>8</sup> they appear weak in the Raman spectra.

**High pressure solid.** When crystallized under ca. 20 kbar pressure in the diamond cell, the IR spectrum of CNCO was drastically different from that of the low temperature solid. Thus, the high pressure crystal will consist of molecules in the *a*-conformation as concluded for CCN. In addition to *trans*-1-bromo-2-chlorocyclohexane,<sup>1</sup> also *trans*-1,4-dichloro- and dibromocyclohexane<sup>22</sup> have been found to crystallize in the *ee* and *aa* conformations upon cooling and pressurizing, respectively. Obviously, several factors, including the molar volume and intermolecular forces in the "axial" and "equatorial" crystals, the enthalpy ( $\Delta H$ ) and the entropy ( $\Delta S$ ) difference as well as the barrier between the conformers are some of the deciding factors. Probably, the molar volume of the axial conformers was smaller than for the equatorial, thus favouring the *a* conformations under high pressure.

**Spectral features.** For CNCO we were able to attribute the IR and Raman bands with considerable certainty. Bands present in the low temperature crystal and absent in the high pressure crystal should be *e*, with *a* bands the other way around. On the other hand, bands present in both the crystals should be common to the conformers. It can be seen from Table 3 that approximately 12 *e*-bands, 10 *a*-bands, and 16 *a*+*e* bands were attributed below 1400  $\text{cm}^{-1}$ .



This indicates that some fundamentals have remained unobserved or they are hidden by other fundamentals. Correlation splitting of 5–10  $\text{cm}^{-1}$  was observed for certain bands in the low temperature IR spectrum, while the resolution might not have been sufficient in the high pressure IR or the low temperature Raman spectra in which larger slits were employed.

Because of the many atoms and low symmetry ( $C_s$  or  $C_1$ ) the fundamental frequencies for both conformers should be highly mixed and attributions to specific vibrational motions very approximate. Comparison of CNCO and CCN with the monohalocyclohexanes,<sup>11</sup> reveals close similarities in the spectra, regarding positions and intensities of the bands. In CNCO, the very strong IR band at 2255  $\text{cm}^{-1}$  with a very weak Raman counterpart is undoubtedly the  $\text{N}=\text{C}=\text{O}$  asymmetric stretch. Due to incomplete data (diamond absorption, low Raman intensity) it cannot be ascertained if this band is common to both conformers. The symmetric  $\text{N}=\text{C}=\text{O}$  stretching mode, expected<sup>17</sup> around 1450  $\text{cm}^{-1}$ , will be mixed with the  $\text{CH}_2$  scissoring frequencies. The bands at 780 and 759  $\text{cm}^{-1}$  are tentatively assigned as the C–N stretches and as observed for the halocyclohexanes, the  $e$ -band is at higher frequency than the  $a$ -band.

Alkyl isocyanates<sup>17</sup> have characteristic  $\text{N}=\text{C}=\text{O}$  bending modes and the bands at 650 and 580  $\text{cm}^{-1}$  are assigned as the out-of-plane and the in-plane  $\text{N}=\text{C}=\text{O}$  bending mode, respectively, both common to the  $e$  and  $a$  conformers.

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