Conformational Equilibria of Cyclohexylethene (Vinylcyclohexane) Investigated by Infrared and Raman Spectroscopy

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Sablinskas, V., Klaeboe, P., Nielsen, C. J., Polavka, J. and Spielbüchler, P., 1992. Conformational Equilibria of Cyclohexylethene (Vinylcyclohexane) Investigated by Infrared and Raman Spectroscopy. – Acta Chem. Scand. 46: 732–742.

The IR spectra of cyclohexylethene were investigated in the vapour and in the liquid at ambient temperature, and as an amorphous solid and as a crystal at low temperatures (140–14 K) in the region 4000–200 cm^{-1}. IR spectra of cyclohexylethene, matrix-isolated in argon and nitrogen, were recorded at 14 K, using a hot nozzle technique during deposition. Raman spectra of the liquid were obtained at various temperatures and spectra of the amorphous and crystalline solids were recorded.

The spectral data were interpreted in terms of two conformational equilibria, one between *equatorial* (*e*) and *axial* (*a*) vinyl, giving an enthalpy difference $\Delta H°$ (*a*–*e*) = 6.8 ± 1.0 kJ mol^{-1} in the vapour (matrix) and 8.2 kJ mol^{-1} in the liquid. Owing to restricted rotation around the C(cyclohexane) – C(vinyl) bond, two conformers (*syn* and *gauche*) for equatorial vinyl were anticipated, and $\Delta H°$ (*gauche*–*syn*) = 0.8 ± 0.3 kJ mol^{-1} in the liquid were obtained. However, the matrix spectra suggested the *gauche* conformer to be more stable in argon by ca. 1.1 kJ mol^{-1}, with a barrier *gauche*–*syn* below 10 kJ mol^{-1}.

The stable conformers of cyclohexylethene were estimated from molecular mechanics calculations, and the energies of the conformational minima were calculated by *ab initio* calculations. Force constant calculations were carried out for each conformer as an aid for the assignments. The IR and Raman spectra were tentatively interpreted in terms of *e, syn; e, gauche* and *a, syn*.

Cyclohexylethene crystallized sluggishly at ca. 145 K, and both the *e, syn* and *e, gauche* conformers were present in the crystal lattice, possibly in a 1 : 1 ratio. The presence of lattice modes of an annealed amorphous solid at ca. 130 K suggested quasi-crystallinity.

A number of monosubstituted cyclohexanes have been studied by vibrational spectroscopy, including cyano- and isocyanocyclohexane,[1] isocyanato- and isothiocyanatocyclohexane,[2] ethynylcyclohexane,[3] bicyclohexyl[4] and cyclohexyl azide.[5] The *equatorial* conformer is more stable than the *axial* in the liquid state and in solution for these compounds, and the *equatorial* conformer is generally present in the crystals. Exceptions are cyanocyclohexane, which crystallizes axially both at low temperature and at high pressure, and isocyanocyclohexane, which is present axially in the high-pressure crystal.[1] When the side group (X) lacks cylindrical symmetry, additional conformers will appear owing to restricted rotation around the C–X bond, giving rise to *anti* (or *gauche* conformers as was observed for bicyclohexyl.[4]

We have studied cyclohexane substituted with ethene and with allene, forming cyclohexylethene ($C_6H_{11}CH{=}CH_2$) and cyclohexylallene ($C_6H_{11}CH{=}C{=}CH_2$). Our results for cyclohexylallene were reported very recently.[6] A stable and a metastable crystal, each containing a separate *equatorial* conformer were formed, and very complete spectral results could be extracted for this compound. Cyclohexylethene (abbreviated as CHE) was previously investigated in solution by an NMR technique,[7–9] and the conformational stabilities of the equatorial conformers were estimated from *ab initio* calculations.[10] No studies of CHE have to our knowledge been made by vibrational spectroscopy, and neither the vapour nor the crystalline state has been investigated. A full account of our results of CHE will be given in the present paper. In spite of the similarities with ethynylcyclohexane[3] (adding two hydrogens to $C_6H_{11}C{\equiv}CH$) and with cyclohexylallene[6] (subtracting one carbon), the conformational results for CHE are quite different from those for these compounds.

Experimental

The sample of CHE was a commercial product from Aldrich. It was purified by double distillation under reduced pressure, and the purity was checked by preparative gas chromatography.

The IR spectra were obtained with FTIR spectrometers, models 88 (4000–400 cm^{-1}) and 114c (600–100 cm^{-1}) from

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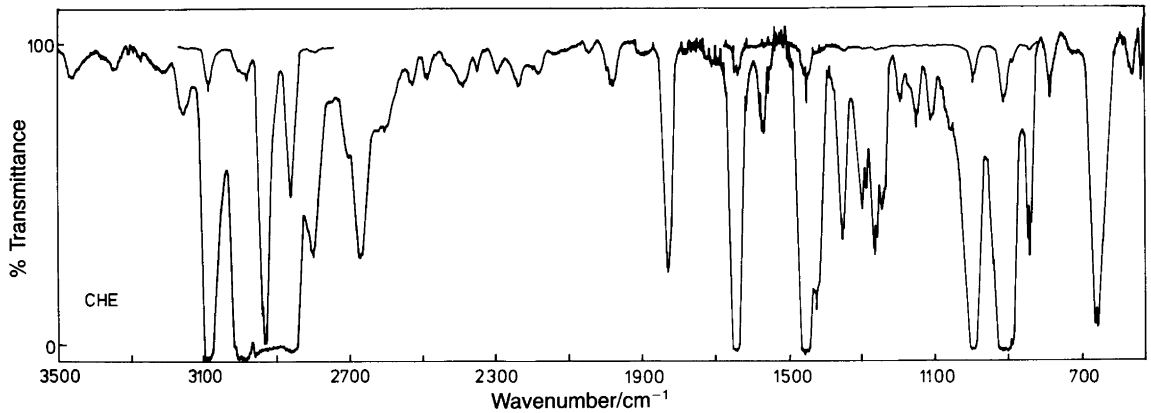

Fig. 1. IR vapour spectrum of cyclohexylethene (CHE) under full pressure, in a multiple reflection cell with approximately 2 m path and in one of 10 cm path.

Bruker, and on a dispersive spectrometer, model 225 (4000–200 cm^{-1}) from Perkin-Elmer. The vapour was studied in a 20 cm cell with polyethylene windows, in a 10 cm cell with KBr windows and at various path lengths (7–2 m) in a multiple reflection cell with KBr windows. Conventional sealed liquid cells with KBr windows were employed in the mid-IR, and 2 mm thick vacuum tight cells with polyethylene windows were used in the far-IR range (below 400 cm^{-1}). Cryostats with CsI windows (mid-IR) and with polyethylene outer windows and a silicon inner window (far-IR), cooled with liquid nitrogen, were employed for obtaining spectra of the amorphous and crystalline solids. Additional IR spectra of the liquid, amorphous and crystalline solids were recorded in a cryostat (model DN 1704) from Oxford Instruments, cooled with liquid nitrogen. Finally, a closed-cycle helium cooler (Displex unit, see below) was employed for recording spectra of the amorphous and crystalline solids in the 100–14 K range. A diamond anvil cell combined with a 4× beam condenser was employed for the high-pressure IR spectra, and the sample was visually inspected in a polarization microscope between each recording.

IR spectra of CHE in argon and nitrogen matrices in the ratio 1 : 500 were obtained at ca. 14 K, using a cryostat (Displex model CSW-202 from Air products) with CsI windows. The inlet system was fitted with an electrically heated nozzle of quartz, and the vapour–matrix gas mixtures were heated to 300, 500 and 700 K before being quenched on the cold window. After the spectra had been recorded, the argon and the nitrogen matrices were annealed to 38 and 34 K, respectively, and the IR spectra were recorded again.

Raman spectra were recorded with a Dilor RTI 30 spectrometer, interfaced to an IBM PC/2 computer, and excited by a Spectra Physics model 2000 argon ion laser. The sample was studied at various temperatures as a liquid in a capillary tube of ca. 2 mm inner diameter, surrounded by a Dewar and cooled with gaseous nitrogen,[11] and in the Oxford cryostat (see above). Additional Raman spectra of a solid deposit on a copper finger, cooled with liquid nitrogen, were recorded, in which the sample was annealed to temperatures close to the melting point.

Attempts were made to obtain clathrates[12,13] of CHE in thiourea, but no clathrates were ever formed by conventional procedures. Differential scanning calorimetry (DSC) curves were recorded in cooling and in heating cycles between 273 and 110 K, with a Mettler TA 3000 system, using both slow and fast cooling and heating rates.

Results

A large number of IR and Raman spectra of CHE were

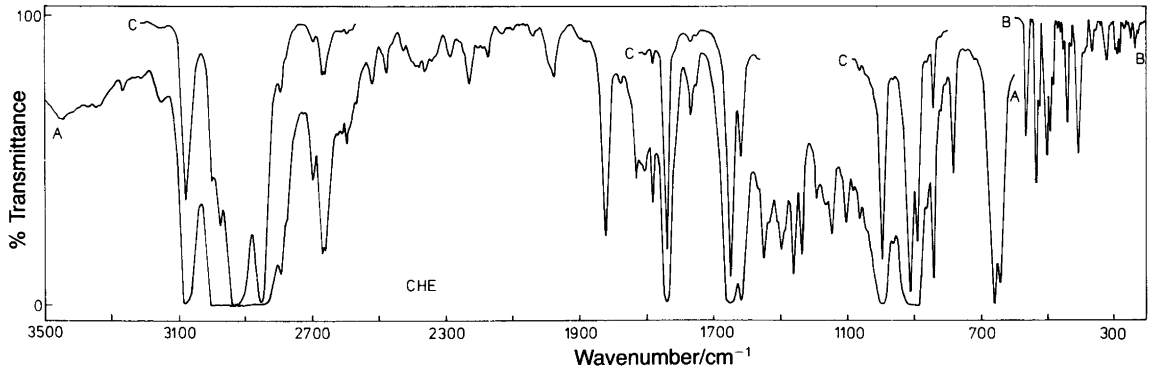

Fig. 2. IR spectrum of CHE as a liquid (3500–200 cm^{-1}): (A) 0.4 mm path, KBr; (B) 1 mm path, polyethylene and (C) 0.05 mm path, KBr.

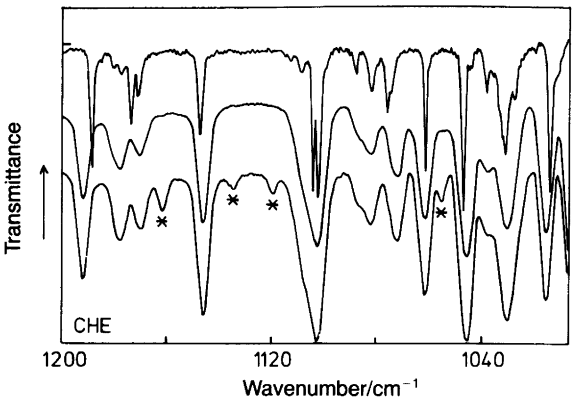

Fig. 3. IR low-temperature spectra of CHE in the 1200–1000 cm^{-1} range, showing amorphous (lower curve), annealed (middle curve) and crystalline (upper curve) samples. The bands vanishing in the annealed amorphous solid and in the crystalline solid are shown by asterisks.

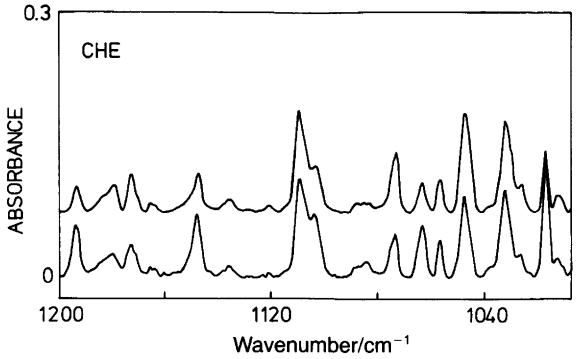

Fig. 5. IR spectra in the range 1200–1005 cm^{-1} of unannealed (lower curve) and annealed (upper curve) CHE in an argon matrix (1:500) at 14 K.

recorded at various temperatures and in different states of aggregation, and some of these are shown in the present paper. An IR spectrum of the vapour is shown in Fig. 1, and the liquid at ambient temperature is presented in Fig. 2. A far-IR spectrum (600–200 cm^{-1}) of the liquid is also included in Fig. 2. CHE has a melting point at ca. 147 K, but crystallization is quite difficult to achieve at these low temperatures, requiring exactly the right conditions and a long annealing time. The IR curves of Fig. 3 (1200–1005 cm^{-1}) shows an amorphous solid formed by shock freezing the vapour on a CsI window at 14 K (bottom), an amorphous solid which was annealed to 130 K and recorded at 14 K (middle) and finally a crystalline solid, annealed to 143 K and recorded at 14 K (top). An unannealed IR spectrum (3500–500 cm^{-1}) of CHE, matrix-isolated in argon (1 : 500), recorded at 14 K, using a nozzle temperature of 300 K, is given in Fig. 4. An unannealed as well as an annealed argon matrix spectrum in the 1200–1005 cm^{-1} range appear in Fig. 5. Corresponding unannealed IR curves in argon matrices were recorded at the nozzle temperatures 300, 500 and 700 K, and the 1200–1005 cm^{-1} regions of these are displayed in Fig. 6.

Attempts were made to crystallize the compound at high pressure. The liquid was filled into a spacer of bronze with 0.4 mm diameter in the diamond anvil cell (DAC). Although pressures as high as 100 kbar were employed, CHE did not crystallize under pressure, as easily observed in a polarization microscope.

A complete Raman spectrum of CHE as a liquid is given in Fig. 7, and a crystalline spectrum, obtained by prolonged annealing at 140 K, recorded at 85 K is shown in Fig. 8. The region for external modes (200–15 cm^{-1}) is shown in the Raman for an unannealed amorphous, an annealed amorphous and for a crystalline solid in Fig. 9. Additional Raman spectra of liquid CHE were recorded at seven temperatures between 300 and 135 K. Three of these curves from the liquid (at 300, 230 and 135 K), together with two spectra of the crystal (at 135 and 85 K), are reproduced in Fig. 10, showing the 1675–1625 cm^{-1} range. The IR and Raman spectral data of CHE in different phases are collected in Table 1.

Conformations

It is assumed *a priori* that two types of conformational equilibria are present in CHE (Fig. 11): (1) *equatorial (e)–axial (a)* positions of the vinyl group relative to the cyclohexane ring and (2) conformers due to restricted rota-

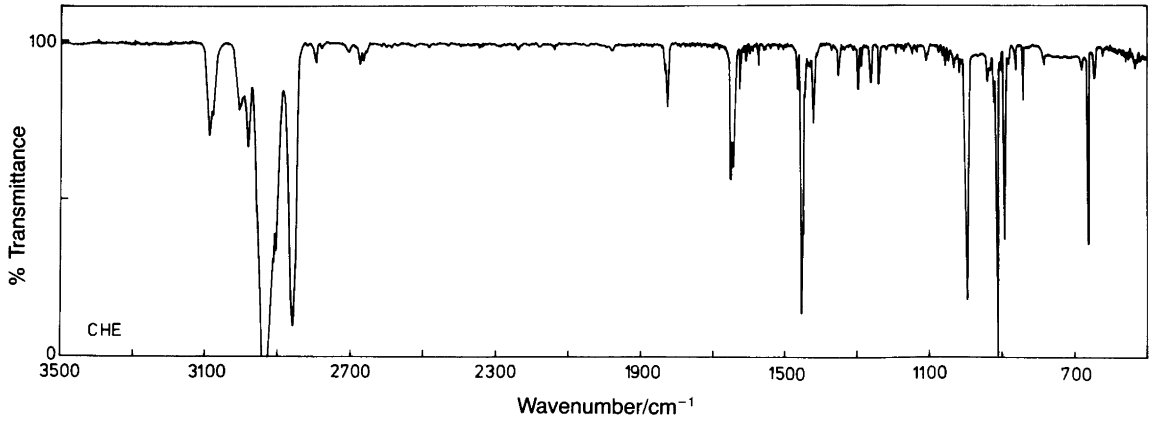

Fig. 4. IR spectrum of unannealed CHE in an argon matrix (1)500) at 14 K.

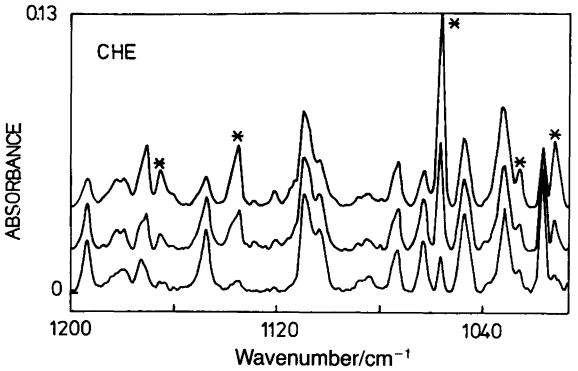

Fig. 6. IR spectra in the 1200–1005 cm^{-1} range of unannealed CHE in argon matrices (1:500), deposited at the nozzle temperatures 300 (lower curve), 500 (middle curve) and 700 K (upper curve), at 14 K. The bands enhanced at higher temperatures and vanishing in the low-temperature solids have asterisks.

tion of the C–C (=) bond. The latter rotation gives rise to a potential minimum in *syn* [the C=C bond eclipsing an *axial* C–H bond for (*e,syn*) or eclipsing an *equatiorial* C–H bond in (*a,syn*)] both with C_s symmetry. An additional *gauche* position, rotated ca. 120° from *syn*, is expected for the equatorial conformer. An (*e,anti*) position (C_s symmetry), involving eclipsing of two C–H bonds, suggested from molecular mechanics was not supported by *ab initio* calculations. In principle both the *equatorial* and the *axial* vinyl groups may occupy *syn* and *gauche* positions, giving rise to the four conformers shown in Fig. 11. The scheme is quite similar to that drawn for cyclohexylallene.[6] It can immediately be seen from a model that the *a,gauche* conformer is highly improbable because of the strong repulsion between the terminal vinyl hydrogens and the axial cyclohexane hydrogens, ruling out *a,gauche* as a realistic alternative. In cyclohexylallene, the two terminal allene hydrogens lie in a plane perpendicular to the terminal hydrogens in vinyl, reducing the repulsion considerably compared to CHE, but still making *a,gauche* much more unfavourable than *a,syn*.

Calculations. Molecular mechanics calculations on CHE were carried out with the two programs MAXIMIN 2[14] and MM2,[15] and both gave the lowest enthalpy conformer in

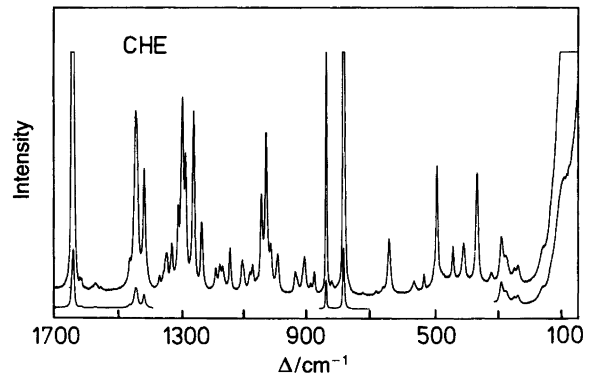

Fig. 7. Raman spectrum (1700–50 cm^{-1}) of liquid CHE at room temperature.

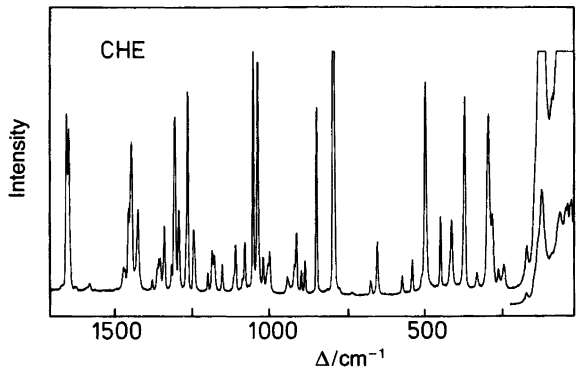

Fig. 8. Raman spectrum (1700–15 cm^{-1}) of crystalline CHE, recorded at 130 K.

e,syn, followed by *e,gauche* with an additional minimum in *e,anti*. In the axial conformation a minimum was found at *a,syn*. We also made *ab initio* calculations with the programs Gaussian 88, 3-21G and 6-31G[16] for determining the conformational energies of the optimized minima. While the second minimum *e,gauche* was calculated to be 5.4 kJ mol^{-1} above the lowest minimum at *e,syn*, the *gauche–syn* barrier is 6.2 kJ mol^{-1} and the *gauche–gauche* barrier 5.4 kJ mol^{-1}. The energy difference between *e,syn* and *a,syn* was estimated to be 14 kJ mol^{-1}, all results from the 3-21G calculations. With the larger basis set of the 6-31G *e,gauche* was calculated to be 4.5 kJ mol^{-1} above *e,syn*, whereas *a,syn* was 88.8 kJ mol^{-1} higher in energy than *e,syn*.

We anticipated *a priori* a much higher $\Delta H°$ difference between the *e* and the *a* conformers than between the *syn* and *gauche*. The present results reveal that the enthalpy differences for the *e–a* equilibrium is approximately 6.8 kJ mol^{-1} (calculated to be 8.8 kJ mol^{-1}) and for the *syn–gauche* equilibrium 0.8 kJ mol^{-1} (calculated to be 4.5 kJ mol^{-1}). Thus the 6-31G set gave a reasonably good agreement with the *a,syn–e,syn* energy difference, whereas the

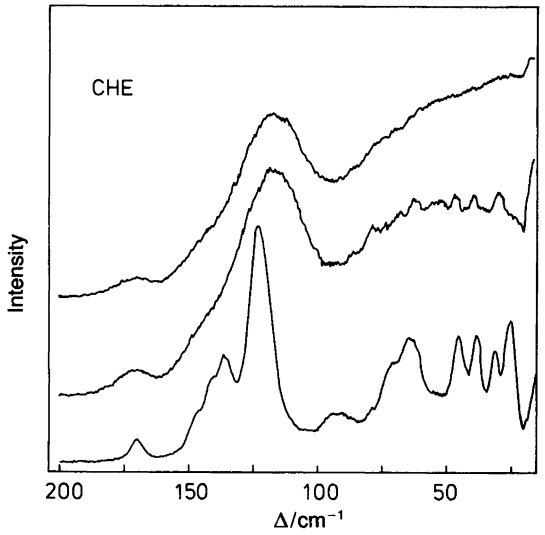

Fig. 9. Raman spectra of unannealed, amorphous (upper curve), annealed, amorphous (middle curve) and crystalline (lower curve) CHE in the 200–15 cm^{-1} range, recorded at 85 K.

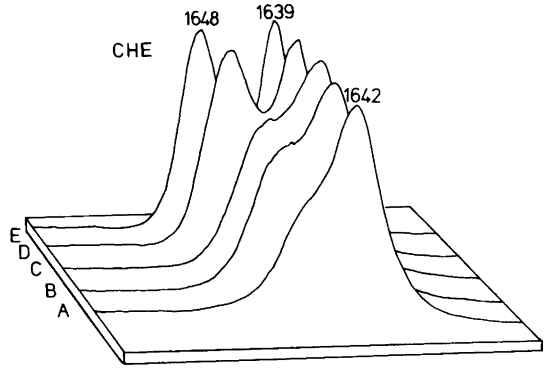

Fig. 10. Raman curves of CHE recorded in the 1675–1625 cm^{-1} range: liquid at 300 (A), 230 (B) and 135 K (C) and in the crystalline state at 135 (D) and 85 K (E).

e,gauche–e,syn energy was much too high in the calculations. However, distinct improvements were obtained by increasing the basis set from 3-21G to 6-31G. The molecular mechanics calculations (see above) gave enthalpy differences far from the experimental values.

The 6-31G basis set is apparently too simple to provide a satisfactory agreement with the experimental enthalpy difference *e,gauche–e,syn*; however, it gave a good agreement with the expected geometry, since only the four conformers of Fig. 11 were predicted. The basis set STO-3G with a simplified geometry, used for *ab initio* calculations 10 years ago by de Maré,[10] gave three *equatorial* minima, *syn, gauche* and *anti,* with an enthalpy difference of more than 20 kJ mol^{-1} between the two low-energy conformers.

The barrier to the *e–a* equilibria is expected to be ca. 40 kJ mol^{-1}, typical for conversions of the cyclohexane ring.[17] A much lower value of 11.8 kJ mol^{-1} was recently determined for the *syn–gauche* barrier in the compound 3-fluoro-2-methylpropene,[18] somewhat related to CHE. The highly different barriers between the *e–a* and the *syn–gauche* equilibria are important for interpreting the low-temperature IR and Raman spectra. The thermodynamic equilibria in amorphous solids and in matrices will be obtained at much lower temperatures for the *syn–gauche* than for the *e–a* equilibria.

Axial–equatorial *equilibrium.* The six IR bands at 1165, 1135, 1121, 1056, 662 and 681 cm^{-1}, present in the amorphous solid at 14 K, vanished completely when the sample was annealed to ca. 140 K. The amorphous solid was intially formed by shock-freezing the vapour (at room temperature) at 14 K. Supposedly, the conformational equlibrium of the vapour will be maintained in the amorphous solid after quenching, maintaining the room-temperature concentration of the *axial* conformer. This is very likely, since the barrier to conversion of the cyclohexane ring[17] is of the order of 40 kJ mol^{-1}, and a rapid conversion of *axial* to *equatorial* conformer will require annealing temperatures of more than 120 K, easily seen from plots of ΔE (barrier) versus T/K.[19] The complete disappearance of the bands requires a relatively large $\Delta H°$, and the high annealing temperature of 140 K indicates a large barrier. Therefore, it seems quite certain that the vanishing bands listed above are due to the *axial* conformer of CHE. This assumption is confirmed by the fact that these bands are also present in the IR spectra of CHE matrix isolated in argon and nitrogen, formed by quenching the vapour mixtures at room temperature on the cold window. Moreover, these bands remain (Fig. 5) after annealing to the highest possible temperatures of these matrices (34–36 K).

The enthalpy difference $\Delta H°(a-e)$ can be determined by the variable-temperature method of the matrix-isolated spectra. In Fig. 6 the IR curves, recorded at 14 K, are obtained with nozzle temperatures of 300, 500 and 700 K. The intensities of the bands attributed to the *axial* conformer (see above) are enhanced with temperature in the curves for 300, 500 and 700 K compared to the remaining bands, which are assigned as *equatorial.* Three *axial* bands, situated at 1056, 1135 and 1165 cm^{-1} in the argon matrices, were selected and ratioed against the supposedly *equatorial* bands at 1032, 1109 and 1240 cm^{-1}.

The *axial/equatorial* band intensities were plotted versus $1/T$ in conventional van't Hoff plots, and the points fitted with straight lines in the least-squares approximation. As is apparent from Fig. 12, the straight lines were quite parallel, giving the $\Delta H°(a-e)$ values of 6.8, 6.9 and 6.8 kJ mol^{-1}, leaving 6.8 ± 1.0 kJ mol^{-1} as an averange in the argon matrix (vapour). An uncertainty of 1 kJ mol^{-1} includes the systemic errors and not merely the accidental errors in these plots. This value for CHE lies within the experimental uncertainty of $\Delta H°(a-e) = 6.5 \pm 1.5$ kJ mol^{-1}, determined for cyclohexylallene in an argon matrix.[6] It is significant that when these band pairs are investigated in the unannealed argon or in the nitrogen matrices their intensities do not change appreciably after annealing. Since the highest annealing temperatures are ca. 34–36 K in the matrices, the barrier is undoubtedly higher than ca. 10 kJ mol^{-1}, in good agreement with the assumed barrier height for the *a–e* equilibrium. In addition to the three *axial* bands at 1056, 1135 and 1165 cm^{-1}, two bands at 1219 and 1012 cm^{-1} were observed in the argon matrices. They were also assigned as *axial* bands, but were not detected in IR spectra of the solids because of overlap with *equatorial* bands.

An independent determination of $\Delta H°$ was carried out from Raman spectra of CHE as a liquid, recorded at seven temperatures between 300 and 170 K (Fig. 13). It can be seen that the Raman band at 825 cm^{-1} diminishes in intensity upon cooling compared to the band at 880 cm^{-1}. From a van't Hoff plot of the intensity ratio between the 825 and 880 cm^{-1} bands, $\Delta H°(a-e)$ of the liquid was determined to be 8.2 kJ mol^{-1}, somewhat higher than the value from the matrix (vapour).

The equilibrium between the equatorial and the axial vinyl groups in CHE was previously determined by ^{13}C NMR spectroscopy at low temperatures, giving (indirectly)[7] $\Delta G°(a-e) = 7.03 \pm 0.25$ kJ mol^{-1} at 173 K in CD_2Cl_2 solution and $\Delta G°(a-e) = 6.2$ kJ mol^{-1} in CD_2Cl_2–CS_2 mixed solutions.[8] From our present $\Delta H°(a-e)$

Table 1. Infrared and Raman spectral data[a] for cyclohexylethene (vinylcyclohexane).

Infrared					Raman		Assignment			
Vapour	Ar matrix, 300 K[b]	N_2 matrix, 300 K	Liquid, 300 K	Crystal, 85 K	Liquid, 300 K	Crystal, 85 K	*e,syn* No.[c]	*e,syn* Calc.[d]	*e,gauche; a,syn* Calc.[d]	Tentative description[2]
3093s 3087s } A′ 3083s	3091s 3081s	3091s 3082s	3081m	3085s 3078s 3073s	3082m,D	3079m	$\nu_{1,2}$	3097, 3079		=CH_2 asym. str. =CH str.
3004m 2995m	3008m 3004m	3011m 3007m	3000w	3000s 2987m	3002s,P	2998m	ν_3	2998		=CH_2 sym. str.
2982s	2983s	2988s 2982s		2979s 2973m	2993s,P	2991m	ν_4	2978		CH str.
2943s 2936s } A 2932s	2935vs	2939vs 2932vs	2926vs	2930vs	2937vs,P	2934s	ν_5	2926		CH_2 asym. str.
					2921vs,P	2919s	$\nu_{6,7,36-37}$	2919–2914		CH_2 asym. str.
					2896m,P	2886m	$2\nu_{13}$			overtone
2863s	2860vs	2870sh 2860vs	2852s	2866s 2448vs	2853vs,P	2845s	$\nu_{8-10,38,39}$	2861–2851		CH_2 sym. str.
1645s	1650s↑ + 1644s↓ −	1649s↑ + 1642s↓ −	1639s	1642s 1637s	1650sh P↑ 1642vs P↓	1648s 1639s	ν_{11}	1645	1640′	C=C str.
	1623m	1625m			1619w,P	1621vw	$\nu_{54}+\nu_{55}$			comb.
	1596m 1590m	1601m 1597s					$\nu_{20}\nu_{33}$			comb.
1571m	1573m	1578m	1573m	1583m 1568m	1572w,P	1573w	$2\nu_{55}$			overtone
	1464s	1464m	1461s	1464m 1460s	1466w,P	1466w 1459w	$\nu_{12,40}$	1458, 1448		CH_2 sciss.
1453vs	1452s 1449sh 1445sh	1452vs 1445sh 1436sh 1433m	1448vs	1451s 1445s 1442s 1439s	1446s,D	1449m 1439s 1422sh	$\nu_{13,14,41}$	1440–1427		CH_2 sciss.
1427mC	1421s	1422s	1417s	1417s	1419s,P	1418m	ν_{15}	1395		=CH_2 sciss.
1357m 1354m } A 1349m	1371w 1369w 1358w	1368m	1367m	1368m	1367w,D	1371w 1357w	$\nu_{16,42}$	1392, 1389		CH bip. CH_2 wag.
	1352s	1352m 1348sh		1350m 1347m 1344m	1349m,D	1351m 1347m	$\nu_{43,44,17}$	1352–1343		CH_2 wag.
	1333w	1332w	1333sh	1332m 1330m	1331m,D	1333w	ν_{18}	1319		CH_2 wag.
	1314m	1314w	1309w	1307m 1303m	1311m,P↑	1311m			1303′	
1297m	1297s	1299s	1296m	1295s 1295s	1298s,P	1301s 1298sh	ν_{19}	1263		=CH rock.
1288wC	1287s	1288s	1288w	1286s	1289s,D	1287m	ν_{45}	1306		CH_2 twist.
1266m 1263m } A 1258m	1261s	1262s	1260m	1265s 1262m 1259s 1257m	1262s,D	1263sh 1258s	ν_{46}	1248		CH_2 twist.
1245m 1240m } B	1240s	1240s	1236m	1239s 1238s 1236m 1232m	1237m,D	1241m 1237m	ν_{20}	1239		CH_2 twist.
	1219m↑	1220m↑							1222″	
1194m 1190m } B	1193m↓ −	1194m↓ −	1192m	1188m	1193m,D	1193m	ν_{21}	1220		CH_2 twist.
	1182w 1179w	1183w 1180w		1180w 1177w 1173m	1181m,D	1180m	ν_{47}	1182		CH_2 twist.
	1170m↑ + 1165m↑	1173m↑ + 1165m↑	1169w 1165sh	1170m *	1171m,P	1172m	ν_{22}	1144	1143″	=CH_2 rock.
1153m 1149m } A 1144m	1149m↓ −	1149w↓ −	1146m	1147m	1147m,P↑	1146m			1134′	
	1135m↑ 1121w↑	1137m↑ 1120w↑	1135vw 1121vw	* *					1139″ 1116″	
1112m 1108m } A 1103m	1109m 1103sh	1108m 1103sh	1103m	1108w 1104s 1102s	1107m,br,P	1110w 1103m	ν_{48}	1101		CH_2 rock.
	1089w 1084w	1089w 1083w	1082w	1088m 1081m	1083w,sh	1082w	ν_{13-33}			comb.
1075m	1072m↑ + 1062m↓ − 1056s↑	1075m↑ + 1062m↓ − 1057m↑	1075w 1061m	1076m 1061s *	1075m,D	1073s	ν_{49}	1072	1071′ 1080″	CH bop.
1054vw	1046m↑ + 1032w↑	1047↑ + 1032w↑	1043w	1047m	1047s,D↓	1047s	ν_{23}	1026	1033″	CH_2 rock.

Cont.

Table 1. Cont.

Infrared					Raman		Assignment			
Vapour	Ar matrix, 300 K[b]	N_2 matrix, 300 K	Liquid, 300 K	Crystal, 85 K	Liquid, 300 K	Crystal, 85 K	*e,syn*		*e,gauche; a,syn* Calc.[d]	Tentative description[2]
							No.[c]	Calc.[d]		
				1038w 1031m 1027m 1020w						
1032w	1026w	1026w	1030sh		1032s,D	1032s	ν_{24}	1017		CH_2 rock.
	1017m 1012m↑	1017m 1013↑	1014m	1014m	1017m,D	1014	ν_{25}	999	1011″	C–C_α str.
				1003s		1005m				
998s 992s B	994vs	1001s 996vs	993vs	998vs 995s 992s	995m,D	1000m 993m	ν_{50}	1052		$=CH_2$ bop.
942wC	940s 933m	940s 932m	933m	936s 931s 925s	938m,P	936m	ν_{26}	907		CH_2 rock.
917vs 914vs A 910vs	911vs	914vs	910vs	922m 921m 918s 910vs	911m,D	916m 906s	ν_{51}	922		$=CH_2$ wag.
889s	904sh 892vs	902m 892vs	890s	910m 891s 889s	890vw	892m	ν_{52}	915		CH_2 rpck.
	884m	884m		881s 879m	880m,P	880m	$\nu_{53,27}$	891, 885		ring str.
	860s↑	860m↑	862	*					869″	
846s 841s A 836s	841s	841s	840m	843s 841s 840s	842vs,P	843s	$\nu_{54,28}$	852, 833		ring str.
	825w↑				825m,D↑				813″	
				790m						
789m 784m B	785m	785m	784m	788m 785m 783m	787vs,P	790vs 784sh	$\nu_{55,29}$	792, 762		ring str.
725w			723vw		725vw,P	730vw	$\nu_{31}+\nu_{59}$			comb.
	680m↑	683m↑	681w	*	685w↑				680″	
				671s						
664s 665s B	663vs	665vs 662s	661s	668s 665s	660w,D	668w	ν_{56}	676		$=CH$ bop.
	644m	643m 640m	642m	647m	644m,P	648m	$\nu_{33}+\nu_{58}$			comb.
563m	561m		566m	565m	567m,br,D	566w	$\nu_{57}+\nu_{60}$			comb.
537mC	532m	533m	535m	535m 532m	535m,P	534w	ν_{30}	546		C–C_α=C bend.
				505m						
	493m	492m	492m	494m 492m 489m	493s,P	504sh 492s	ν_{31}	515		ring def.
			441m	445m 441m	443m,D	443m	ν_{57}	461		ring def.
				411m						
			405m	409m 406s	408m,P	414m 407m	ν_{32}	411		ring def.
			365w		366s,P	365s	ν_{33}	371		ring def.
			318w		319w,D	327w	ν_{34}	306		ring def.
			288w		288m,P	294s 289s	ν_{58}	303		ring def.
			278w		273m,D	276m	$\nu_{35}+\nu_{60}$			comb.
			247w		247m,P	258w	$\nu_{31}-\nu_{59}$			comb.
			232w		235m,P	239w	ν_{59}	228		ring C–C^α bop.
					156sh	167w	ν_{35}	143		ring-vinyl bip.
						144w 133m				External modes
					95sh	117vs	ν_{60}	68		vinyl tors.
						89w 69m 59m 42m 36m 29w 23m				External modes

[a]Weak bands in the regions 4000–3100 and 2800–1700 cm^{-1} have been omitted. [b]Temperature of matrix-CHE vapour before deposition on the cold window. [c]Numbering for *e,syn* conformer. [d]Force field from Ref. 3, [e]From the largest term in the potential-energy distribution (PED). [f]Abbreviations: s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder; P, polarized; D, depolarized; A, B, C denote band contours; ↑ and ↓, bands which increase or decrease in relative intensity with increasing (nozzle) temperature; + and −, bands which increase or decrease in relative intensity upon annealing at ca. 35 K; *, bands which disappear upon annealing of amorphous solid at 130 K; (′), bands which belong to *e,gauche*; (″), bands which belong to *a,syn* conformers; C_α denotes the carbon of the vinyl group attached to the cyclohexane ring.

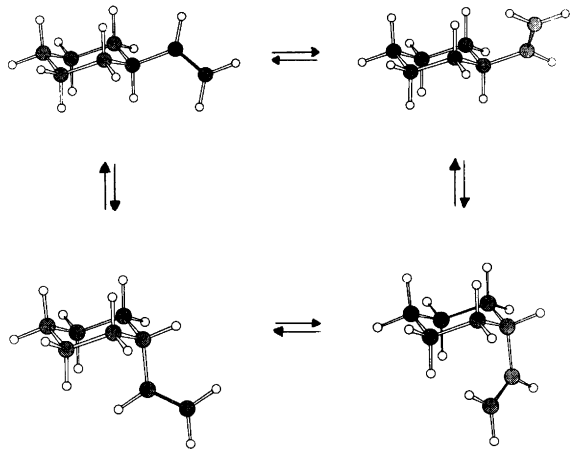

Fig. 11. The four predicted conformations of CHE; *e,syn* (C_S), upper left; *e,gauche* (C_1), upper right; *a,syn* (C_S) lower left and *a,gauche* (C_1) lower right.

value of the liquid (8.2 kJ mol^{-1}) and an average $\Delta G°$ value[7,8] of 6.6 kJ mol^{-1} from the NMR spectra in solution at 173 K, the thermodynamic functions for CHE can be determined at other temperatures. From the relation $\Delta G° = \Delta H° - T\Delta S°$ the values $\Delta S° = 1.16$ J mol^{-1} K^{-1}, $\Delta G°(a-e) = 6.45$ kJ mol^{-1} and $K = 13.6$ were obtained at 298 K.

Syn–gauche *equilibrium.* It can be seen from Fig. 10 that in liquid CHE two Raman bands are present in the C=C stretching region, a band at 1642 with a shoulder at 1650 cm^{-1}. The spectra recorded at different temperatures reveal that the 1650 cm^{-1} band is enhanced relative to 1642 cm^{-1} on cooling. However, the intensity variation with temperature is much smaller than that observed for the three band pairs described above. Since these two bands overlap considerably, it was necessary to employ curve resolution techniques to treat them in a van't Hoff plot. Another band pair in the Raman spectrum of the liquid, at 1047 and 1147 cm^{-1}, which were well separated, behaved in the same way; the 1047 cm^{-1} band increased in intensity at lower temperatures. Both these band pairs were treated in van't Hoff plots in the temperature range form 295 to 135

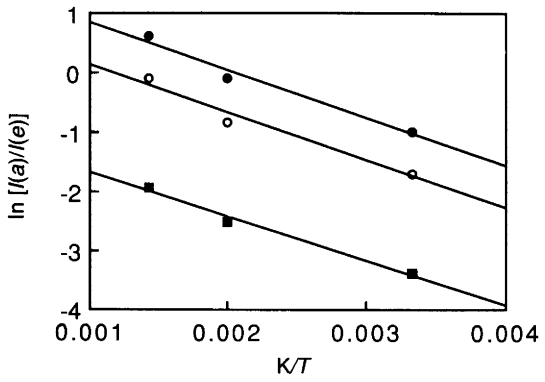

Fig. 12. van't Hoff plots of three band pairs (*axial/equatorial*) from the argon matrix spectra, (●) 1056 (*a*)/1032 (*e*) cm^{-1}, (○) 1135 (*a*)/1109 (*e*) cm^{-1} and (■) 1165 (*a*)/1240 (*e*) cm^{-1}.

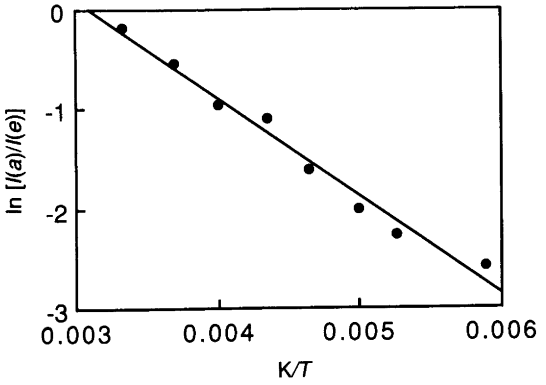

Fig. 13. van't Hoff plot of 825 (*a*)/880 (*e*) cm^{-1} band from Raman liquid spectra.

K, giving the same values $\Delta H°(gauche-syn) = 0.8 \pm 0.3$ kJ mol^{-1}. We have interpreted these features as due to a *syn–gauche* equilibrium of the *equatorial* vinyl group in CHE. These values from the pure liquid agree very well with the NMR results of de Maré and Lapaille,[9] based upon the coupling constants as a function of temperature, giving $\Delta H° = 0.85$ and 0.89 kJ mol^{-1} in the solvents tetrachloroethylene and deuteroacetone, respectively.

The two band pairs discussed above are also present in the IR, and they are well separated as sharp bands in the unannealed matrix spectra. When the argon matrices were annealed to 34–36 K the bands at 1650 and at 1046 cm^{-1} were enhanced compared to those at 1644 and 1149 cm^{-1}, as anticipated. The conformational equilibrium of the unnealed matrix reflects the nozzle temperatures varying from 300 to 700 K. After annealing, however, assuming the barrier to be sufficiently low, the equilibrium will be that of the annealing temperature, leading to a displacement to the more stable conformer.

When the unannealed matrix spectra recorded at different nozzle temperatures were analyzed, the equilibrium was unexpectedly displaced towards the bands at 1650 and 1049 cm^{-1} with higher nozzle temperatures, suggesting that these bands belong to the high-energy conformer. From van't Hoff plots derived from the intensity variations with the temperatures 300, 500 and 700 K of the band pair

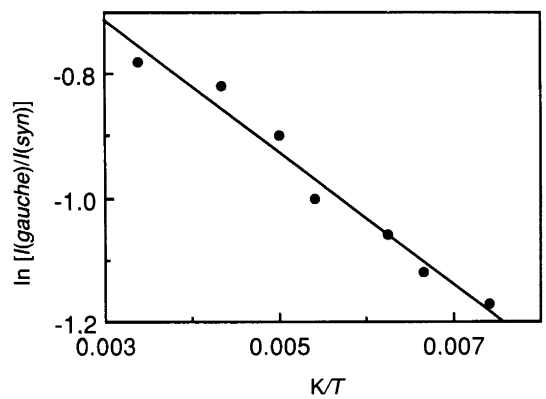

Fig. 14. van't Hoff plot of the 1147 (*gauche*)/1047 (*syn*) cm^{-1} band pair from Raman liquid spectra.

1149/1046 cm^{-1}, the enthalpy difference was $\Delta H°$ (*gauche–syn*) = -1.1 kJ mol^{-1}.

This result is contrary to that from Raman spectra of the liquid, as well as from the annealing experiments, since the more stable conformer in the liquid (presumably *syn*) is the less stable in the matrices. Moreover, the enthalpy difference $\Delta H°$(*gauche–syn*) derived from the matrices is ca. 1.9 kJ mol^{-1} lower than the $\Delta H°$ of the liquid and of the solution.[9] These results can only be explained by certain assumptions: (1) the enthalpy differences *gauche–syn* in the vapour and in the liquid are quite different and (2) specific interactions take place between one of the conformers and the matrix.

Large changes in $\Delta G°$ and $\Delta H°$ from the vapour to the liquid are observed when the conformers have very different dipole moments. In these cases the polar conformer is stabilized in the liquid compared to the vapour. An extreme example is provided by 1,2-dicyanoethane, for which the conformational equilibrium is highly displaced towards the *anti* conformer, without a dipole moment, in the vapour[20] and towards the *gauche* conformer, with a very large dipole moment, in the liquid.[21] However, the *syn* and *gauche* conformers of CHE have nearly equal dipole moments, as shown by molecular mechanics as well as the *ab initio* calculations. It was observed that the solutions of CHE in CCl_4, $CHCl_3$, CH_2Cl_2 and CH_3CN, a series of solvents with increasing polarities, gave nearly equal intensities of the Raman bands at 1047 (*syn*) and 1147 cm^{-1} (*gauche*).

We have previously observed that one conformer can be stabilized in argon, the other in nitrogen matrices, leading to quite different $\Delta G°$ as well as $\Delta H°$ values between the conformers in the two matrices (examples are 1,1,2-trichloro-2,3,3-trifluorocyclobutane[22] and ethylazide[23]). The intensity variations of CHE are observed on very weak bands, and the observations of the nitrogen matrix were inconclusive. However, the *e,gauche* conformer of CHE may be stabilized in the argon matrix, explaining the large difference in $\Delta H°$(*e,gauche* – *e,syn*) between the liquid and the vapour (argon matrix). The intensity variations of the *e,gauche* and the *e,syn* bands with temperature (Fig. 6) and the results of the annealing experiments (Fig. 5) in the argon matrices still seem contradictory for CHE and are not yet fully understood.

Low-temperature crystal spectra

Generally, the IR and Raman spectra of a crystalline solid have fewer vibrational modes than those of the vapour, liquid or amorphous states in a molecule with conformational equilibria, since only one conformer will be accomodated in the crystal lattice. Bands belonging to additional conformers will therefore vanish when a liquid crystallizes. In some rather unusual cases two or more crystals can subsequently be formed, and each crystal contains molecules with a separate conformer. This was the case for cyclohexylallene,[6] for which a stable crystal contained molecules with the allene group in *syn* (*anti*), whereas a metastable crystal contained molecules in *gauche*, both being *equatorial* to the cyclohexane ring. In bicyclohexyl[4] at least three stable crystals were formed, one of them containing *anti*, one *gauche* and the third a mixed *anti–gauche*, first believed to be a plastic,[4] but more recently[24] interpreted as a liquid-crystalline phase.

The DSC curves gave independent proof that CHE does not crystallize readily, and with the low cooling and heating rates (0.5 K min^{-1}) no phase transitions were observed between 270 and 100 K. At the faster cooling rates of 5 and 10 K min^{-1} very small exothermic humps were observed around 127 and 118 K, suggesting partial crystallization. In the IR or Raman cells, crystals of CHE were formed only after long and tedious efforts. Crystallization was equally difficult to achieve when a liquid was cooled or when an amorphous solid formed by shock freezing the vapour on a cold window at 80 or 15 K was annealed to temperatures just below the melting point at 147 K. However, with considerable patience and several hours annealing time, low-temperature crystallization occurred for thin capillaries on a CsI plate, and on a copper block or in a glass capillary for Raman measurements.

It appears from the figures, however, that the crystal spectra of CHE were quite similar to those of the liquid recorded at temperatures just above melting. It is particularly significant that the band pair at 1648 and 1639 cm^{-1}, as well as the band pair at 1146 and 1047 cm^{-1}, both remain in the crystal spectra. The bands situated at 1648 and 1047 cm^{-1} in the Raman spectra of the crystal, both assigned to the more stable conformer, increased in intensity on crystallization compared to those at 1639 and 1146 cm^{-1}. Additional experiments revealed that the intensity ratio between the Raman crystal bands of each band pair did not change noticeably in the temperature range 140–80 K.

We are forced to draw the conclusion that the two equatorial conformers, *syn* and *gauche*, are present in the crystal of CHE. It is significant that the ratio between *syn* and *gauche* changed from the liquid to the crystalline states, since small but distinct changes in band intensities occurred on crystallization. However, no intensity variations appeared on further cooling, although the bands attributed to the *syn* and *gauche* conformers both became narrower and better separated. These features support the assumptions that both the *e,syn* and *e,gauche* conformers exist in a stoichiometric ratio in the unit cell, independent of the temperature. No trace can be seen in the crystal spectra of bands assigned to the *axial* conformer. With a difference in $\Delta H°$ between the *axial* and *equatorial* conformers of around 6–7 kJ mol^{-1}, only a few percent of the *axial* conformer will be present around the melting point of 147 K. In addition, the *axial* conformer molecules are probably not accomodated in the crystal lattice.

Various examples have been reported in the literature of cases when a mixture of two or more conformers does not simplify upon solidification. However, in many of these cases there are doubts if the compound really crystallizes or

merely exists as an undercooled liquid or as an amorphous solid, in which the conformers are in thermodynamic equilibrium. As an example isocyanocyclohexane[1] had both the *equatorial* and *axial* conformers in the low-temperature solid, apparently since no crystal was ever formed. When the sample was pressurized in a diamond anvil cell, however, only the *axial* conformer was present.[1] Another example is 1,1,2-trichlorotrifluoroethane (freon 113), which crystallized around 125 kbar to give the C_1 conformer, whereas both the C_1 and C_s conformers were present in the low-temperature solid, probably since no crystallization occurred.[25]

The Raman spectra of CHE revealed beyond doubt that, after tedious annealing (see above), the sample formed crystals. Before annealing, the sample appeared isotropic, but changed to anisotropic after crystallization, clearly seen from the reflected laser beam. Even more significant is the appearance of a number of distinct peaks in the Raman spectrum below 150 cm^{-1} (Fig. 10), characteristic of external lattice modes. Therefore, we feel confident that the low-temperature solid of CHE is a real crystal. At least one example of a molecule in which two different conformers are present in the unit cell is known to us. Thus, for 3,3,5,5,8,8,10,10-octamethyl-3,5,8,10-tetrasilacyclodeca-1,6-diyne $[-(CH_3)_2Si-C{\equiv}C-Si(CH_3)_2(CH_2)-]_2$ it was observed by X-ray crystallography[26] that two different conformers of this molecule are present, with three molecules in the unit cell of space group P_1. Two molecules of identical boat conformations, having C_{2v} symmetry, are situated in a general position relative to the symmetry centre. An additional conformer with a symmetry centre (C_{2h}) is positioned in the symmetry centre, giving a stoichiometric ratio of 1:2 in the crystal.[26] A similar arrangement might be present in the crystals of CHE. Since we lack X-ray data, no conclusions can be drawn either for the space group or for the number of each conformer molecules in the unit cell. The spectral intensities suggest that the ratio between the *syn* and the *gauche* conformers might be 1:1 in the crystal.

When the capillary filled with CHE was rapidly cooled to 80 K and annealed at ca. 130 K for 30 min, the sample still appeared amorphous and the crystallization described above had not taken place. The Raman spectrum above 150 cm^{-1} appeared identical to that observed before annealing. In the low-frequency region, however, a number of weak bands were detected (Fig. 9) which were present neither in the liquid at ambient temperature nor in the unannealed amorhous solid below 120 K. It appears from Fig. 9 that the bands are similar to those of the crystal, but with lower intensities and less structure. The bands are undoubtedly caused by external lattice modes and may belong to a 'quasi-crystalline' solid or an amorphous solid which is partly crystalline, while still appearing isotropic.

It is well known that cyclohexane itself, as well as certain substituted cyclohexanes like fluoro- and chlorocyclohexane, both have plastic phases. It is our experience that the existence of a plastic phase often leads to 'difficult' crystallizations (e.g. in fluoro-[27] cyano-[1] and isocyanocyclohexane[1]). However, we were not able to detect a plastic crystalline phase in CHE, either in the DSC measurements or in the low-temperature spectra.

Spectral interpretation

Force fields have been derived for a series of substituted cyclohexanes and presented in various papers.[1,3,28] The force field for cyano-[1] and ethynylcyclohexane[3] was directly adopted to CHE, with additional force constants introduced for the vinyl group. Tetrahedral angles with C–C and C–H distances of 1.54 and 1.093 Å, respectively, were employed for the cyclohexane ring. In the vinyl group the C=C bond was given the value 1.308, the C–H bonds 1.085, the C–C bonds 1.51 Å and the C=C–H angles 122°. Separate calculations were made for the *e,syn* (C_s symmetry), for *e,gauche* (C_1 symmetry), rotated 120° from *syn* and for *a,syn* (C_s symmetry), shown in Fig. 11.

The results of the normal-coordinate analysis for the supposedly most stable conformer (*e,syn*) are given in Table 1, together with the experimental results. Tentative assignments of the observed IR and Raman bands to the fundamentals of the *e,syn* conformer are shown. The potential-energy distribution (PED) for each mode of the *e,syn* conformer is not listed in Table 1 for the sake of brevity. Instead an approximate description of the fundamentals in terms of the major contribution to the PED is given.

Since the bands of the *e,syn* conformer could not be separated in the the crystal, no reliable means could be found to decide which bands are specific to *e,syn*, which are specific for *e,gauche* and which are overlapping for *e,syn* and *e,gauche*. Some additional bands of low intensities were found for the *axial* conformer (probably *a,syn*), and they can frequently be identified, since they disappear at low temperatures as a consequence of the large $\Delta H°$ values. For cyclohexylallene[6] the asignments could be made with high confidence, since each of the two equatorial conformers was identified in separate crystals. These crystals revealed that a large number of *syn* and *gauche* bands for cyclohexylallene overlapped,[6] as we have assumed for CHE.

The *e,gauche* bands from the variable-temperature spectra are also listed in Table 1, together with the relatively few cases of *axial* bands (*a,syn*), and we have, for the sake of brevity, only included the calculated wavenumbers for the vibrational modes of the more unstable conformers (*e,gauche* and *a,syn*), which were observed in the spectra. Calculated wavenumbers for all the vibrational modes of the two unstable conformers (*e,gauche* and *a,syn*) and the potential-energy distribution can be obtained from the authors on request.

Some of the fundamentals of CHE can with certainty be attributed to characteristic group frequencies of the vinyl group. Thus, the three CH stretches of vinyl, expected above 3000 cm^{-1}, were assigned to the bands at 3091, 3081

and 3006 cm^{-1} in the argon matrix, the two former overlapping in the liquid spectra. The two IR bands at 1650 and 1644 cm^{-1} in the argon matrix are undoubtedly the C=C stretching modes for the *e,syn* and the *e,gauche* conformers, also present in the IR and Raman liquid and crystal spectra. While the CH_2 scissoring modes of the cyclohexane ring overlap around 1466 and 1446 cm^{-1} (liquid, Raman), the $=CH_2$ scissor is observed at 1419 cm^{-1}. The IR and Raman bands around 1319 cm^{-1} are tentatively attributed to the =CH in-plane bending ν_{18} of species *a'*, whereas the bands around 911 cm^{-1} are assigned to the *a''* out-of-plane wagging mode of $=CH_2$ (ν_{51}). Finally, the bands at 660 cm^{-1} may tentatively be attributed to the =CH wag ν_{56} of species *a''*.

The bands observed around 680 cm^{-1} in the matrices, disappearing in the low-temperature solid, are undoubtedly due to an *a,syn* fundamental. This fits reasonably well with the 'spectral indicator', proposed[29] for the *axial* conformer in alkyl-substituted cyclohexanes to be found between 595 and 650 cm^{-1}, although an additional *e,syn* band was found in this region around 660 cm^{-1}.

The most stable conformer in the liquid is attributed to *e,syn*, in agreement with the results of the NMR results in solution.[9] Since *syn* and *gauche* have statistical weights of one and two, respectively, this leads to approximately 40 % *syn* and 60 % *gauche* at room temperature [from ΔH° (*gauche*−*syn*) = 0.8 kJ mol^{-1}], which seems reasonable judging from the IR and Raman band intensities. The opposite assignments (*gauche* being the more stable) would lead to approximately 25 % *syn* and 75 % *gauche*, which seems unreasonable from the observed band intensities.

Acknowledgements. The authors are grateful to Anne Horn for assistance with the spectral recordings and to Kari Bjerkelund for the DSC measurements. Financial support to V.S. from the Royal Norwegian Council for Scientific and Industrial Research (NTNF), to J.P. from the Norwegian Research Council for Science and the Humanities (NAVF) and to P.S. from IAESTE is gratefully acknowledged.

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Received December 23, 1991.