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Vibrational Spectra and Conformations of 1-Chloro-2,2,3,3-tetrafluorocyclobutane and 1-Cyano-2,2,3,3-tetrafluorocyclobutane

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The IR and Raman spectra of 1-chloro- and 1-cyano-2,2,3,3-tetrafluorocyclobutane were recorded in various phases and at different temperatures, including IR matrix spectra in argon and in nitrogen matrices using the hot nozzle method.

Both compounds had two conformers in the vapour and liquid states, while they crystallized as one distinct conformer. All the bands vanishing in the crystal spectra had low intensities in the vapour and liquid states. The matrix spectra of both compounds contained only one conformer at 13 K as well as at 4.8 K, revealing that the high-energy conformers were not trapped. Thus, a barrier below 2.0 kJ mol^{-1} from the *axial* to the *equatorial* (Cl or CN substituents) conformers is suggested for both molecules. The enthalpy difference $\Delta H°$ between the conformers in the liquid was 3.4 ± 0.7 kJ mol^{-1} for the chloro compound and 3.9 ± 0.9 kJ mol^{-1} for the cyano compound. From *ab initio* calculations with the 3-21G* and 6-31G* basis sets, the enthalpy differences 4.2 and 6.2 kJ mol^{-1}, respectively, were obtained for the chloro compound.

Fairly complete assignments of the e-conformer spectra were made for both molecules with the aid of force-constant calculations derived from scaled *ab initio* force constants for the chloro, and on transferred force constants for the cyano compound.

It is well documented that in monosubstituted cyclobutanes, e.g. fluoro-[1], chloro-,[2,3] bromo-,[2,4] cyano-[5,6] and methylcyclobutane,[7] the conformational equilibria are strongly shifted towards the equatorial conformer, making it difficult even to prove the existence of a high-energy (axial) conformer.

In geminally disubstituted cyclobutanes with two different substituents C_4H_6XY, the X and Y atoms compete for the more favourable equatorial position, and the enthalpy difference between the two conformers is fairly small, as was demonstrated when the IR and Raman spectra of 1-chloro-1-fluoro,[8] 1-chloro-1,2,2-trifluorocyclobutane[8] and 1,1,2-trichloro-2,3,3-trifluorocyclobutane[9] were investigated. These compounds were studied in considerable detail, including the recording of matrix isolation spectra with the hot nozzle technique. It was concluded that $\Delta H°$ between the conformers was ca. 2.2 kJ mol^{-1} for 1-chloro-1-fluoro,[8] 2.9 for 1-chloro-1,2,2-trifluoro[8] and 0.9 kJ mol^{-1} for 1,1,2-trichloro-2,3,3-trifluorocyclobutane[9] in the liquid state.

We have found it interesting to extend these studies to include the two title compounds 1-chloro-2,2,3,3-tetrafluorocyclobutane (to be abbreviated TFCLCB) and 1-cyano-2,2,3,3-tetrafluorocyclobutane (TFCNCB). Since all the four fluorines are geminally substituted in the two molecules, they have, to a first approximation, no direct influence on the conformational equilibrium. The equilibria are expected to be quite similar to those of the chloro- and cyano-cyclobutane, highly shifted towards the equatorial position of Cl and CN. However, the puckering angle of the cyclobutane ring and the barrier to conversion will be influenced by the four electronegative fluorine atoms.

In an earlier paper Harris and Yang[10] published the vibrational spectra of TFCLCB, concluding that only one conformer was present. No spectroscopic study of TFCNCB has to our knowledge ever been reported.

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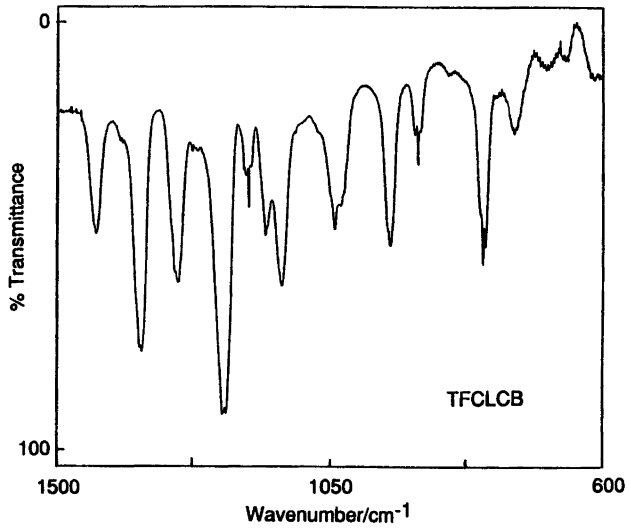

Fig. 1. IR spectrum of TFCLCB as a vapour in the 1500–600 cm^{-1} range; path 10 cm, pressure ca. 10 Torr.

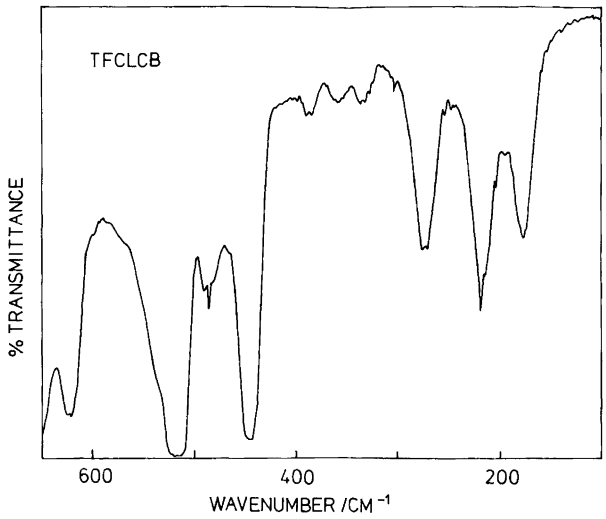

Fig. 2. IR spectrum of TFCLCB as a vapour in the 650–60 cm^{-1} range, path 20 cm, 80 Torr pressure, resolution 2 cm^{-1}, 3.5 and 12 μm Mylar beamsplitters were employed.

Experimental

The sample of TFCLCB was a commercial product from K & K Rare and Fine Chemicals, USA, whereas TFCNCB was delivered by Riedel-de Haën, Germany. Both compounds were shown by analytical GC measurements to be better than 99.5% pure. Their identities were further checked by mass spectrometry. No purification of these compounds was carried out, except for a bulb-to-bulb distillation which removed fluorescent impurities before the Raman recordings.

Infrared spectra of both compounds were recorded on a Bruker model 88 spectrometer and on an evacuable Bruker model 114c FTIR spectrometer, covering the regions 4000–400 and 700–50 cm^{-1}, respectively, as well as on a Perkin-Elmer model 225 grating spectrometer (4000–200 cm^{-1}). The IR spectra of TFCLCB were recorded as a vapour and as a liquid at different temperatures. Spectra of amorphous and crystalline solids at 80 K were recorded in cryostats with inner windows of CsI and silicon. Additional crystal spectra were recorded at high pressure with a diamond anvil cell. Matrix isolation spectra were recorded at 13 K of 1:700 sample-to-matrix ratios employing a Displex unit (model CSW-202) from Air Products. Additional spectra were also studied in a Heliplex HS-4 cryostat from APL, capable of giving 4.8 K at the cold window. Both argon and nitrogen matrices were used. The effect of heating the gas mixtures prior to deposition on the cold CsI window was

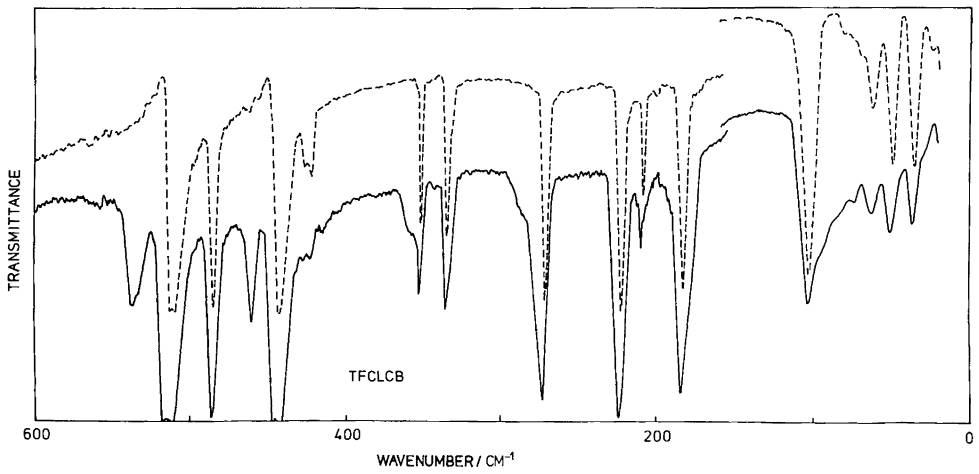

Fig. 3. IR spectrum of TFCLCB in the 600–40 cm^{-1} dissolved in cyclohexane (solid curve) and as an annealed crystal (dashed curve) at 85 K, resolution 2 cm^{-1}.

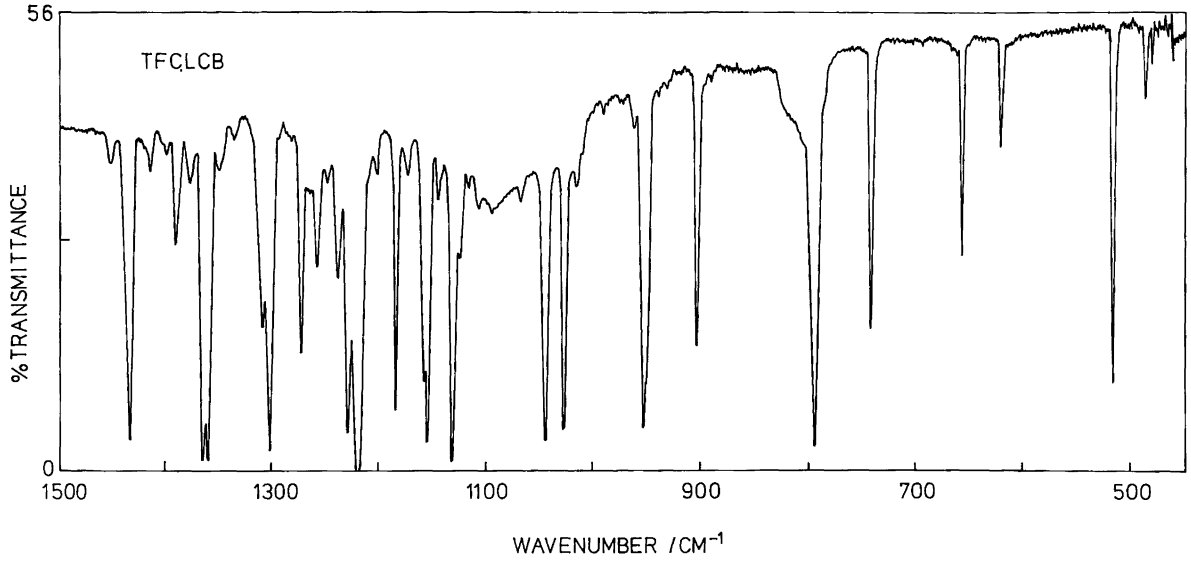

Fig. 4. IR spectrum of TFCLCB in a nitrogen matrix (1:700) before annealing covering the region 1500–400 cm^{-1}, deposited at 14 K.

also studied by passing the gases through an electrically heated quartz nozzle at 450 and 600 K in addition to ambient temperature.

Raman spectra were recorded with a triple monochromator spectrometer from Dilor (model RTI 35) interfaced to the Aspect 2000 data system of the 114c Bruker spectrometer. The samples were illuminated by the 514.8 nm line of a Spectra-Physics model 2000 argon ion laser.

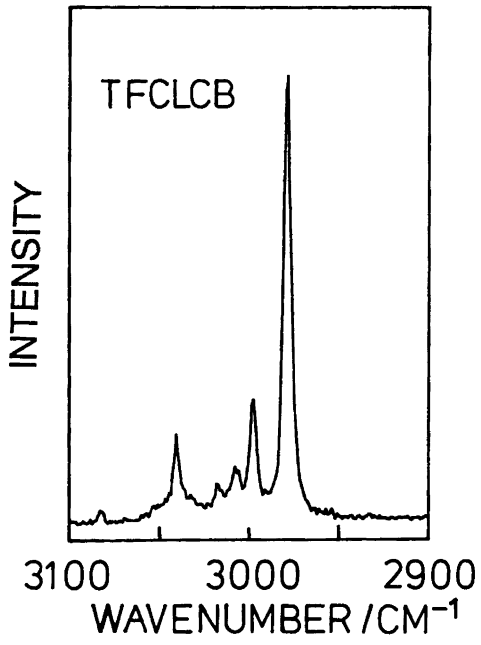

Fig. 5. Raman spectrum of TFCLCB as a vapour in the 3100–2900 cm^{-1} range, with 80 Torr pressure.

TFCLCB was also studied as a vapour in a cell with Brewster angle windows, employing a multiple-pass system from Spex, modified for the Dilor spectrometer. The low vapour pressure of TFCNCB prevented a corresponding recording of this vapour spectrum in the Raman. Both compounds were studied as liquids and as solids in a capillary, surrounded by a Dewar and cooled by nitrogen gas.[11] The liquid samples were also studied with the aid of a cryostat from Oxford Instruments (model DN 1704) cooled with liquid nitrogen. Additional Raman spectra were recorded of the compounds deposited from the vapour phase on a copper finger at liquid-nitrogen temperature. Spectra were obtained before and after annealing the samples to different temperatures below the melting point.

A diamond anvil cell coupled to a 4 × beam condenser from Perkin-Elmer was used for obtaining high-pressure IR spectra. The samples were contained in a hole of 0.4 mm diameter in spacers of bronze and stainless steel of 0.1 mm thickness. The cell was inspected visually in a polarization microscope between recordings, and approximate pressures were estimated from the spring tension and cell geometry.

Differential scanning calorimeter (DSC) curves were recorded in heating as well as in cooling cycles between 290 and 180 K in a Perkin-Elmer scanning calorimeter, model DSC-4 equipped with a thermal analysis data station.

Results

1-chloro-2,2,3,3-tetrafluorocyclobutane (TFCLCB). A mid-IR vapour spectrum of TFCLCB in a cell of 10 cm path is shown in Fig. 1 while a far IR spectrum is given

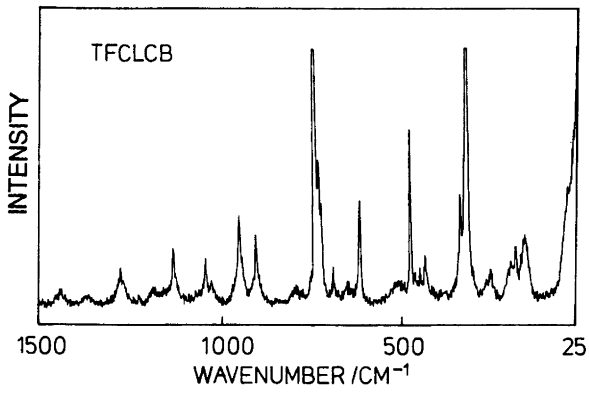

Fig. 6. Raman spectrum of TFCLCB as a vapour in the 1500–40 cm^{-1} range, with 80 Torr pressure.

in Fig. 2. A far IR spectrum of the sample dissolved in cyclohexane and of the annealed crystalline solid, obtained by shock-cooling the vapour on a CsI window at 85 K and subsequent annealing to 140 K was recorded at 85 K and is given in Fig. 3. A survey spectrum of the sample in a nitrogen matrix (unannealed) is known in Fig. 4. Raman spectra of the vapour are given in Figs. 5 and 6, whereas Raman spectra of the liquid and of the crystalline solids are shown in Figs. 7 and 8. The experimental data for TFCLCB, including the assignments, are listed in Table 1.

When the Raman spectra of liquid TFCLCB were recorded at different temperatures ranging from 297 to 193 K, systematic intensity variations of various bands were observed. Certain bands enhanced their relative intensities at higher temperatures and a comparison with the solid-state spectra shows that these bands also vanished from the spectra upon crystallization. Many of these bands were quite weak, and some were observed only in IR or in Raman. The bands in question are marked with asterisks in Table 1.

1-Cyano-2,2,3,3-tetrafluorocyclobutane (TFCNCB). A survey spectrum of TFCNCB as a liquid and in solution is given in Fig. 9 and a comparison of the amorphous and crystal spectra in Fig. 10. An unannealed IR matrix isolation spectrum (argon) is shown in Fig. 11. The far-IR spectra of the sample dissolved in cyclohexane, as an amorphous solid and as a crystal are presented in Figs. 12a, 12b and 12c, respectively. Raman spectra of the liquid and crystal are combined in Fig. 13. The experimental results and spectral interpretations are collected in Table 2.

TFCNCB showed much the same spectral changes with temperature and the same disappearance of some bands upon crystallization as was noted above for TFCLCB. Accordingly, the bands showing this behaviour are also marked with asterisks in Table 2.

High-pressure spectra. Both compounds were studied under pressure in a diamond anvil cell. No significant changes in the IR spectra of TFCLCB or in those of TFCNCB were observed under pressures as high as 50 kbar. In particular, the axial bands which vanished after crystallization at low temperatures remained in the high-pressure spectra. Moreover, the sample did not appear crystalline when observed in the polarization microscope. Apparently, we were not able to crystallize either of the two compounds at high pressure at ambient temperature. It should be noted that for other molecules the situation is different. Thus, in isocyanocyclohexane[12] and in 1,1,2-trichlorotrifluoroethane[13] high-pressure crystallization was achieved even in cases when no low temperature crystals were formed. In certain other molecules with a small enthalpy difference between the conformers, investigated in this laboratory, the low temperature and the high-pressure crystals contained different conformers.

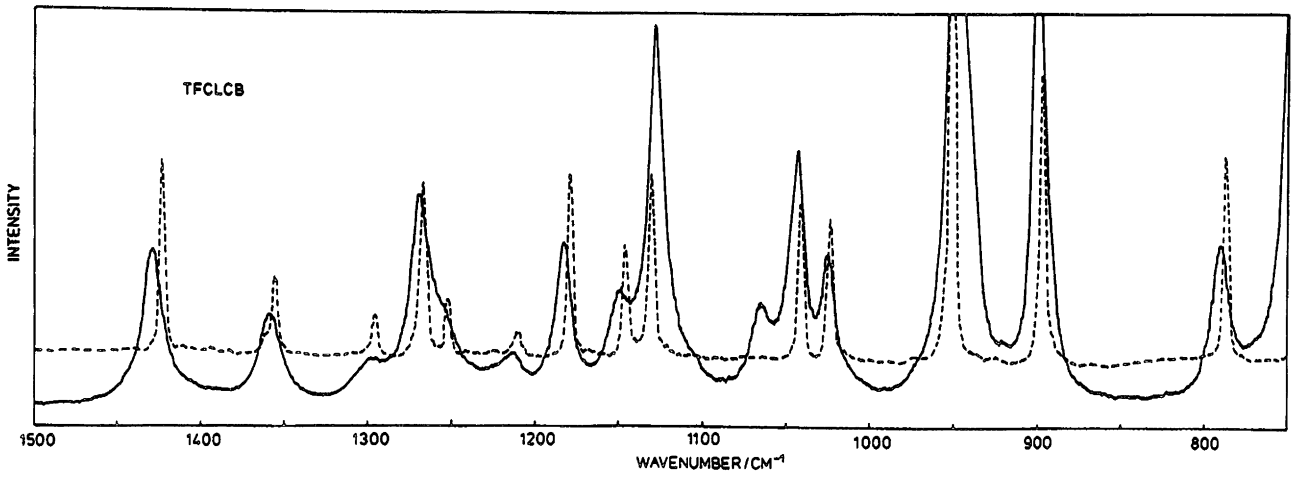

Fig. 7. Raman spectra of TFCLCB as a liquid at 298 K (solid line) and as an annealed crystal at 80 K (dashed line) in the 1500–700 cm^{-1} range.

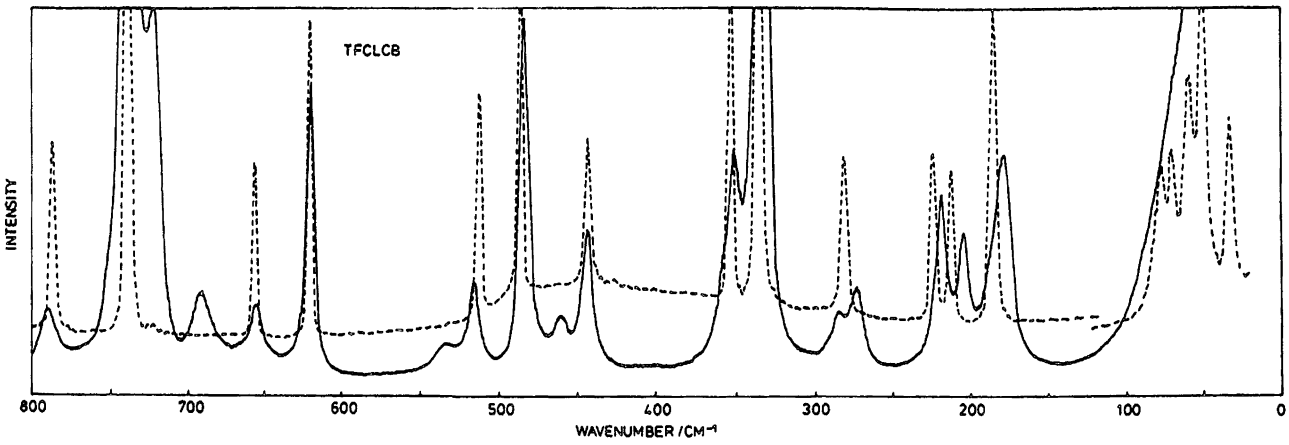

Fig. 8. Raman spectra of TFCLCB as a liquid at 298 K (solid line) and as an annealed crystal at 77 K (dashed line) in the 800–30 cm^{-1} range.

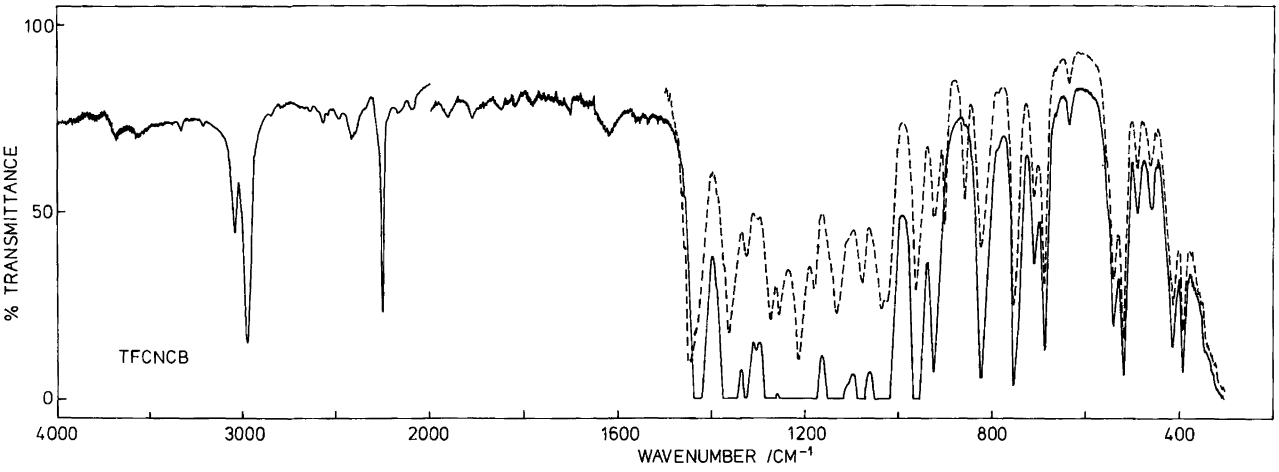

Fig. 9. IR spectrum of TFCNCB in a 0.03 mm cell (solid line) and as a solute in cyclohexane (dashed line), resolution 2 cm^{-1}.

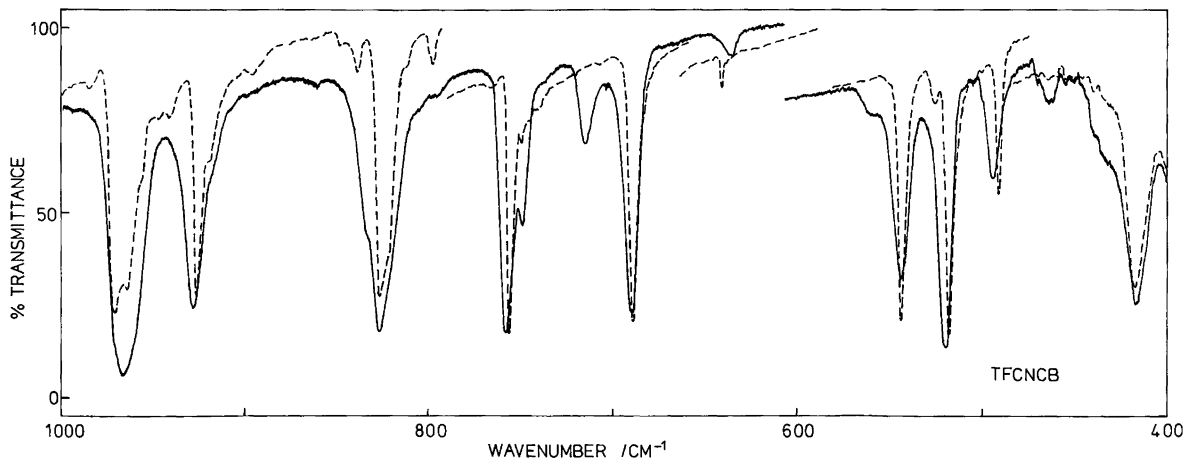

Fig. 10. IR spectra of TFCNCB as an amorphous solid (solid line) and as an annealed crystal (dashed line) at 80 K.

Table 1. Infrared and Raman spectral data for 1-chloro-2,2,3,3-tetrafluorocyclobutane (TFCLCB).

Infrared				Raman			
Vapour	Ar matrix 14 K	Liquid 298 K	Crystalline 77 K	Vapour 298 K	Liquid 298 K	Crystalline 77 K	Assignment
				3079 vw			
3038	3052 vvw[a]	3041 vw	3042 m	3038 m	3040 w		ν_1
				3015 w			
3002				3006 w			
2997	3001 vvw	3000 vw	3013 m	2997 m	3000 w,sh		ν_2
2993	2983 vw	2978 w	2980 m	2979 m	2975 m		ν_3
	2915 vvw	2921 vw	2918 vw				
	2847 vw	2856 vw	2850 vw		2848 vw		
	1451 vw		1440 w				
	1436 w,sh						
1433	1431 s	1429 s	1426 s	1434 w	1430 mw	1424 m	ν_4
	1416w		1405 w				
1395	1397 vw		1392 w				
1388	1386 m	1383 w,sh	1382 ms				
1362	1364 s, 1360 s	1358 s	1360 s, 1352 s	1362 w	1360 w,sh, 1358 mw	1355 mw	ν_5
	1356 w,sh		1341 w,sh				
1311	1310 w		1312 w,sh				
1300	1305 m, 1299 s	1298 s	1300 s		1297 vw	1295 vw	ν_6
1266	1271 m	1269 w	1272 m		1269 m	1267 m	ν_7
	1259 w	1246 w	1248 ms	1255 vw,sh	1252 vw,sh	1252 mw	ν_8
1225	1228 m, 1219 vs	1215 vs	1214 s	1225 vw	1214 vw	1210 w	ν_9
1187, 1183, 1179	1181 m	1184 m	1182 s	1182 m	1183 w	1179 m	ν_{10}
	1172 w		1167 w, 1162 w				
1156, 1152	1154 m, 1151 m	1149 ms	1148 s	1156 vw	1148 w	1146 mw	ν_{11}
1131	1132 m, 1128 s	1128 s	1127 s	1130 m	1127 s	1130 m	ν_{12}
		1116 w,sh					
		1106 w		1102 vvw			
1069	1068 vw	1065 w	*	1060 vvw	1065 mw	*	ν'_{13}
1050, 1043, 1034	1046 m, 1041 ms	1043 ms	1038 s	1044 m	1044 m	1042 m	ν_{13}
	1028 w,sh, 1024 s	1024 m	1022 s	1028 w	1026 m	1023 m	ν_{14}
		990 vw	991 vw				
950	951 m,sh, 950	949 ms	948 s	950 s	949 s	952 s	ν_{15}
					936 w,sh	*	ν'_{15}
908							
903, 899	902 m	899 m	898 ms	904 m	900 m	897 m	ν_{16}
850			840 vw	842 vw			
803, 799, 794	795 s	791 ms	783 s	794 mw	790 w	787 m	ν_{17}
	745 vw,sh	752 w,sh	*		750 vw,sh	*	ν'_{17}
745	743 m	739 m		744 vs, 738 s	740 vs	738 s	ν_{18}
724		725 w,sh	*	724 w,sh	723 w,sh	*	ν'_{18}
691		694 w	*	693 w	692 m	*	ν'_{19}
656	656 m	654 m	655 m	654 w	655 w	656 m	ν_{19}
		634 w,sh					
623, 619, 611	621 w	621 m	620 vs	624 vw,sh, 619 m	621 m	621 s	ν_{20}

Continued.

Table 1. Continued.

Infrared				Raman			
Vapour	Ar matrix 14 K	Liquid 298 K	Crystalline 77 K	Vapour 298 K	Liquid 298 K	Crystalline 77 K	Assignment
		532 w,sh	*		535 w,sh	*	ν'_{21}
520 516 512	516 mw	517 m	515 vs 510 s	516 w	517 m	512 m	ν_{21}
490 485 481		484 w	486 s	484 m	485 m	487 s	ν_{22}
				459 vw	461 w	*	ν'_{22}
443	445 m	445 m	446 s 423 w	445 mw	444 m	443 m	ν_{23}
385		408 w	*	390 vvw	402 vw	*	ν'_{24}
		357 w	*		358 vw,sh	*	ν'_{25}
358		352 w	553 m	350 w	352 m	353 s	ν_{24}
334		334 w	336 m 333 w,sh	337 w 331 s	334 vs	335 s	ν_{25}
		284 w,sh	*	279 w,sh	285 w,sh	*	ν'_{26}
274		273 m	273 s	270 mw	274 m	282 m	ν_{26}
222 218 213		219 m	224 s		219 m	224 m	ν_{27}
		205 w	210 m	216 m	205 m	213 m	ν_{28}
203		197 vvw					
187		184 w,sh	*	201 m	188 w,sh	*	ν'_{28}
177		177 m	185 s	176 m	179 m	186 s	ν_{29}
		173 vw,sh	*		163 w,sh	*	ν'_{29}
						78 ms	
						71 ms	
						55 vw	
				57 w		60 vw	ν_{30}

[a]Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder. An asterisk denotes bands vanishing in the crystal spectra.

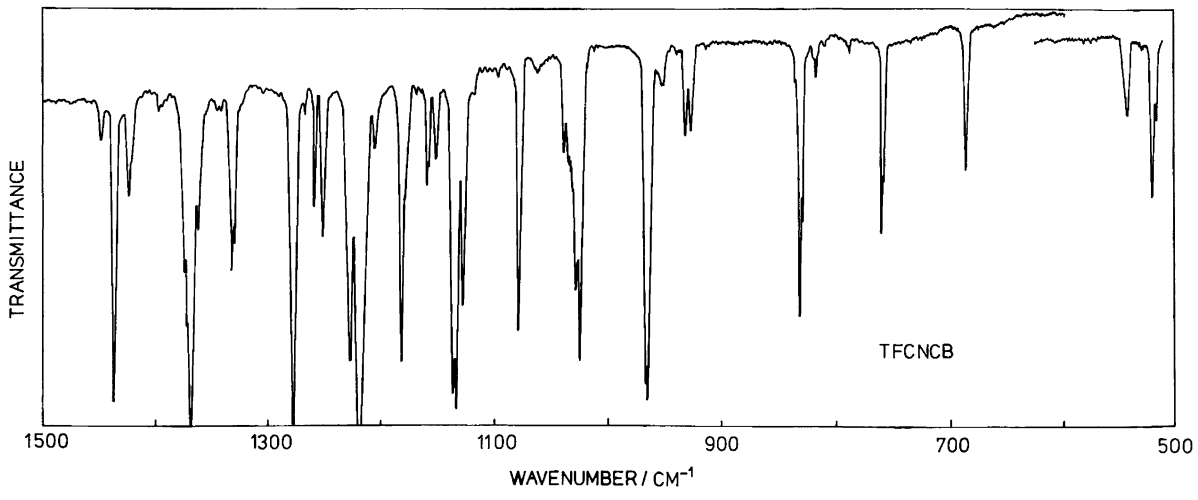

Fig. 11. IR spectrum of TFCLCB in an argon matrix (1:700) at 13 K before annealing covering the region 1500–500 cm^{-1}.

Table 2. Infrared and Raman spectral data for 1-cyano-2,2,3,3-tetrafluorocyclobutane (TFCNCB).

Infrared				Raman		
Vapour	Ar matrix 14 K	Liquid 298 K	Crystalline 77 K	Liquid 298 K	Crystalline 77 K	Assignment
	3041 vvw[a]	3051 w	3056 w	3048 w	3054 m	ν_1
	2991 vvw	2986 w,sh	2995 w	2985 s	2992 m	ν_2
	2984 vvw	2976 m	2976 ms	2978 ms	2976 s	ν_3
		2852 vw		2856 w		
			2289 m		2287 w	
	2264 vvw	2258 m	2263 ms	2260 s	2264 s	ν_4
			2247 vw,sh			
			2214 w	2208 vw	2211 vw	
	1449 w		1445 vw			
1440	1437 m	1431 m	1434 s	1433 mw	1429 m	ν_5
	1424 m					
	1414 vvw		1417 m		1416 vvw	
	1397 w	1394 vw	1396 m			
1366	1369 s	1363 s	1364 m	1364 w	1359 mw	ν_6
1337 1334 1332	1332 m	1329 m	1333 m	1327 m	1327 m	ν_7
			1312 w,sh			
	1304 vw	1304 vw	1302 w	1307 w	*	ν'_8
1281	1277 s	1275 s	1275 m 1268 m	1275 mw	1272 m	ν_8
	1259 m		*	1254 w	1253 vw	ν'_{10}
1249	1252 m	1248 w	1250 vw 1246 m	1242 vw,sh	1242 w	ν_9
			1225 w,sh			
1228 1222	1227 m 1220 vs 1206 w	1208 vs	1214 m	1214 w	1206 w	ν_{10}
1190 1184 1179	1182 m	1185 ms	1184 m	1183 m	1179 w	ν_{11}
	1160 m		1158 m			
	1153 w					
1146	1137 m	1150 vw,sh	1148 m	1147 m	1146 m	ν_{12}
1139	1135 s		1136 m	1136 m,sh	1132 w,sh	
1126	1129 m	1134s	1128 m	1127 s	1127 m	ν_{13}
			1110 w			
1079	1080 m	1080 ms	1086 m	1080 w	1081 m	ν_{14}
	1063 w		1066 m		1066 vw	
		1038 m	1040 w,sh			
	1033 w,sh		1034 w,sh	1038 w,sh	1038 w,sh	
1036	1029 m 1025 s	1027 m	1029 s	1028 m	1028 m	ν_{15}
			984 w			
970 967 959	965 m	963 m	971 m 964 w	966 m	968 m	ν_{16}
			941 w		939 vvw	
931 926	932 m 928 m	925 m	926 m	926 m	924 m	ν_{17}
		865 w	864 vw	861 vvw		
			839 w		840 w	
837 831 829	832 m	825 m	826 m	824 w	822 mw	ν_{18}
			822 w,sh			
	818 w	812 vvw	*	804 w	*	ν'_{18}
		792 w	798 w		793 vvw	
758	761 m	756 m	756 s	756 vs	755 vs	ν_{19}
		751 w,sh	745 w,sh			
		713 w	*	712 w	*	ν'_{20}

Continued.

Table 2. Continued.

Infrared				Raman		
Vapour	Ar matrix 14 K	Liquid 298 K	Crystalline 77 K	Liquid 298 K	Crystalline 77 K	Assignment
689	688 m	689 m	689 m	689 m	689 m	ν_{20}
642		637 w	643 w	638 m	640 m	ν_{21}
		560 vw,sh	*			ν'_{22}
545	542 w	544 m	544 ms	543 m	544 m	ν_{22}
520	520 w,sh 516	522 ms	526 m 520 s	520 m	520 mw	ν_{23}
	496 w	493 w	492 m	493 m	490 mw	ν_{24}
		463 w	*	465 vw	*	ν'_{24}
		429 w,sh	*	429 w,sh	*	ν'_{25}
		412 ms	421 ms 416 w	418 ms	422 m	ν_{25}
		394 m	400 s	395 w	396 w	ν_{26}
		380 w,sh	*			ν'_{26}
		346 m	347 m 344 m	347 m	345 m	ν_{27}
		316 m	319 m	317 m	317 m	ν_{28}
		298 vw	302 vw			
		271 m	278 m 275 m 274 m	273 w	279 w	ν_{29}
		205 m	207 m 195 m	203 vw	206 vw	ν_{30}
		171 m	179 m	173 m	182 m	ν_{31}
		135 m	154 m	141 m	148 w	ν_{32}

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder. An asterisk denotes bands vanishing in the crystal spectra.

Calorimetric measurements. Both TFCLCB and TFCNCB were investigated between 180 and 290 K by means of differential scanning calorimetry. During cooling cycles, both compounds showed substantial supercooling. TFCLCB gave a single peak at 213 K corresponding to a melting transition when heated. TFCNCB on the other hand gave a double peak around 270 K (Fig. 14).

Ab initio *calculations.* Fully optimized geometries and harmonic force fields for the two conformers of TFCLCB have been calculated at the Hartree–Fock SCF level using the Gaussian 90 program[14] (direct SCF) and employing the 3-21G* and 6-31G* basis sets. In addition, the shape of the puckering potential was estimated from a series of 3-21G* calculations, and the result is reproduced in Fig. 15. As can be seen, the *e*-conformer was predicted as the more stable by ca. 4.2 kJ mol^{-1} in this approximation, and the barrier from axial to equatorial was of the order of 1 kJ mol^{-1}. The 6-31G* basis set calculations gave a conformational energy difference of ca. 6.2 kJ mol^{-1}.

The harmonic force fields for the two conformers of TFCLCB (6-31G* basis set) were transformed from Cartesian to suitable internal coordinates and scaled according to the type of internal coordinate using the scheme: $F^{scaled}_{ij} = (x_i x_j)^{1/2} F_{ij}$, where x_i and x_j are scale factors for the diagonal constants. The scale factors used were simply transferred from our recent study of 1-chloro-1-fluoro- and 1-chloro-1,2,2-trifluorocyclobutane.[8] For TFCNCB we merged the *ab initio* TFCLCB force field and the force field of the cyano group in cyanocyclobutane[5] and cyanocyclohexane.[12,15] The resulting wavenumbers for the fundamental vibrations, including the largest terms in the potential energy distribution (PED), are compared with the observations in Tables 3 and 4 for TFCLCB and TFCNCB, respectively.

Discussion

The DSC melting curve for TFCNCB, Fig. 14, shows two unresolved peaks at 267 and 270 K. The larger of the two we associate with the transition from an anisotropic crystalline phase to a plastic crystal and the second with the melting of the plastic crystal. Such a relationship between two energy peaks is quite characteristic of a plastic crystal. Unfortunately, the narrowness of this temperature region has prevented us from obtaining spectra substantiating our interpretation. We were unsuccessful in several attempts in obtaining a spectrum of the plastic phase even in the Oxford cryostat with quite good temperature control. On two occasions we actually began to record a spectrum of this phase, but within a minute or two the sample melted, probably as a consequence of local heating by the argon ion laser. It may be noted that the other substituted cyclobutanes 1-chloro-1,2,2-tri-

fluorocyclobutane[8] and 1,1,2-trichloro-2,3,3-trifluorocyclobutane[9] also show this behaviour in the DSC melting curves, although in both of these cases the plastic crystal temperature range is somewhat larger. Since the DSC curve of TFCLCB only had one transition (melting) no plastic phase seemed to be present for this compound.

When the liquid phase IR and Raman spectra of both compounds are compared with those of the crystal, it is immediately apparent that a number of medium or weaker bands in the liquid-phase spectra are absent in the crystal spectra. For both molecules this has been interpreted in terms of two conformers being present in the liquid, while only one conformer is accommodated in the crystal lattice. A quick glance at the IR or the Raman spectra reveals that the conformer vanishing in the crystal is present in at most 20% abundance in the liquid at room temperature for both of the compounds. A purely qualitative evaluation suggests that the axial vapour bands of TFCLCB are slightly more intense than those of the liquid, suggesting that the equilibrium is somewhat more displaced towards *a* in the vapour.

The systematic intensity variations of distinct bands with temperature are undoubtedly due to a displacement of the conformational equilibrium. As expected, the bands increasing in intensity with higher temperatures are the same as those which vanish upon crystallization, and they are attributed to fundamentals of the high-energy conformer with the chlorine or the cyano group in an axial position. For TFCLCB 12 fundamentals of the axial conformer can immediately be identified: 1065, 936, 750, 723, 692, 535, 461, 402, 358, 285, 188 and 163 cm^{-1}. The remaining 18 fundamentals of the *a*-conformer apparently overlap the *e*-conformer bands which have higher intensities. The force constant calculations carried out for TFCLCB, presented in Table 3, also support the assumption that a large part of the IR and Raman bands belonging to the *a*-conformers overlap those of the *e*-conformers.

Values for the conformational enthalpy difference, ΔH° $(a - e)$, were obtained for TFCLCB from the temperature dependence of the liquid-phase Raman spectra. Intensity data from the temperature range 187–345 K were employed in a standard van 't Hoff plot analysis of axial/equatorial band pairs: 692/655, 692/790, 692/1026 cm^{-1}. Owing to a shortage of non-overlapped bands from the less stable *a*-conformer, the band at 692 cm^{-1} was used in all three pairs. Values of 3.7, 2.7 and 3.8 kJ mol^{-1} resulted, giving an average value of 3.4 kJ mol^{-1} which we estimate to have an uncertainty of about 0.7 kJ mol^{-1}.

Table 3 Observed and calculated frequencies for 1-chloro-2,2,3,3-tetrafluorocyclobutane (TFCLCB).[a]

	Equatorial			Axial		ν(eq) − ν(ax)	
ν_i	Obs.[b]	Calc.	PED	Obs.	Calc.	Obs.	Calc.
1	3040	3033	90 CH_2 assymm st		3034		−1
2	3000[c]	3012	91 α-CH st		3029		−17
3	2975	2969	100 CH_2 symm st		2965		4
4	1430	1426	45 CF_2 st, 39 ring st, 12 CH_2 be		1425		1
5	1358	1359	77 CH_2 be, 10 ring st		1352		7
6	1297	1323	52 CF_2 st, 26 ring st, 11 CH_2 be, 11 rb		1325		−2
7	1269	1295	82 CF_2 st		1302		−7
8	1252	1275	87 CF_2 st		1268		7
9	1214	1233	56 α-CH be		1209		24
10	1183	1167	58 α-CH be		1166		1
11	1148	1137	28 α-CH be, 29 ring st, 18 CF_2 be		1137		0
12	1127	1133	56 CH_2 be, 26 ring st		1115		18
13	1044	1038	32 CF_2 be, 21 ring st, 10 rb	1065	1055	−21	−17
14	1026	1005	47 CH_2 be, 23 CC st, 16 α-CH be		1030		−25
15	949	940	55 ring st, 14 CCl st, 13 CH_2 be	936	923	13	17
16	900	900	36 CH_2 be, 19 CCl st, 15 CF_2 st		895		5
17	790	801	16 CF_2 be, 15 ring st, 15 CCl st, 15 CF_2 st	750	754	40	47
18	740	740	29 CF_2 st, 25 ring st, 11 rb	723	723	17	17
19	655	645	32 CF_2 be, 24 ring st	692	686	−37	−41
20	621	613	23 rb, 15 CF_2 be, 13 CF_2 st		611		2
21	517	511	70 CF_2 be, 11 CCl be	535	538	−18	−27
22	485	490	49 CF_2 be, 11 CH_2 be, 8 CCl st	461	456	24	34
23	444	444	88 CF_2 be, 12 rb		439		5
24	352	348	60 CF_2 be, 14 CH_2 be, 8 CCl be	408[c]	356	−56	−8
25	334	333	77 CF_2 be, 19 rb, 11 CCl st	358	343	−24	−10
26	274	270	69 CF_2 be, 24 ring st, 11 CCl be	285	286	−11	−16
27	219	218	62 CF_2 be, 39 CCl be		214		4
28	205	208	77 CF_2 be, 11 α-CH be, 39 CCl be	188	199	17	9
29	179	172	53 CF_2 be, 45 CCl be	163	183	−16	−11
30	57	69	100 puckering		45		24

[a]Abbreviations: st, stretch; be, bend; rb, ring breath. [b]Raman liquid values, except where otherwise noted, [c]Infrared liquid values.

Table 4. Observed and calculated frequencies for 1-cyano-2,2,3,3-tetrafluorocyclobutane (TFCNCB).[a]

	Equatorial			Axial		ν(eq) − ν(ax)	
ν_i	Obs.[b]	Calc.	PED	Obs.	Calc.	Obs.	Calc.
1	3048	3046	89 CH_2 asymm st		3048		−2
2	2985	3026	90 α-CH st		3042		−16
3	2978	2982	97 CH_2 symm st		2978		4
4	2260	2275	89 CN st, 10 CCN st		2275		0
5	1433	1446	70 CH_2 be, 17 ring st		1439		7
6	1364	1400	33 ring st, 27 CF_2 st, 25 CH_2 be		1399		1
7	1327	1343	36 ring st, 24 α-CH be, 20 CH_2 be		1340		3
8	1275	1314	38 α-CH be, 25 CH_2 st, 19 ring be	1307	1304	−32	10
9	1242	1281	62 CF_2 st, 21 CF_2 be, 16 CH_2 be		1284		−3
10	1214	1241	77 CF_2 st	1254	1233	−40	8
11	1183	1221	56 α-CH be, 15 CF_2 st		1207		14
12	1147	1182	63 CH_2 be, 14 CF_2 st, 11 α-CH be		1164		18
13	1127	1164	50 ring st, 20 CH_2 be		1161		3
14	1080	1082	20 CF_2 be, 17 CH_2 be, 15 CCN st		1100		−18
15	1028	1050	34 CH_2 be, 24 ring st		1077		−27
16	966	979	49 ring st, 15 CCN st		973		6
17	926	934	37 CH_2 be, 23 CF_2 st		924		10
18	824	832	22 CF_2 be, 18 CH_2 be, 16 CF_2 st	804	789	20	43
19	756	751	35 CF_2 st, 25 ring st		739		12
20	689	677	24 CF_2 be, 19 ring st, 14 α-CH be	712	727	−23	−50
21	638	630	23 CF_2 st, 20 ring be		628		2
22	543	535	54 CF_2 be, CCN be	560[c]	551	−17	−16
23	520	509	39 CF_2 be		509		0
24	493	491	51 CF_2 be	465	462	28	29
25	418	412	36 CF_2 be, 32 CCN lin	429	423	−11	11
26	395	391	48 CF_2 be, 32 CNN lin	380[c]	397	−15	−8
27	347	351	87 CF_2 be		355		−4
28	317	332	48 CF_2 be, 21 CCN lin		325		7
29	273	272	79 CF_2 be		284		−12
30	203	205	100 CF_2 be		204		1
31	173	185	40 CF_2 be, 24 CCN lin, 15 α-CH be		180		5
32	141	139	50 CCN be, 31 CCN lin		144		−5
33		72	89 ring be		49		23

[a]Abbreviations: st, stretch; be, bend; rb, ring breath; lin, linear. [b]Raman liquid values, except where otherwise noted. [c]Infrared liquid values.

Independently the band pair 1065 (*a*) and 1044 cm^{-1} (*e*) was treated by a curve-separation procedure; however, the scattering of the intensity data with temperature revealed that this close-lying band pair was less favourable for quantitative calculations.

In TFCNCB there are only eight bands which immediately can be ascribed to the high-energy axial conformer: 1307, 1254, 804, 712, 560, 465, 429 and 380 cm^{-1}. Of these, the 804, 712 and 465 cm^{-1} bands were paired with close-lying equatorial bands at 824, 689 and 493 cm^{-1}, respectively, and analyzed over the 261–296 K range. These bands were not among the strongest in the spectrum, and the measurements, especially those associated with the less abundant conformer bands, had a considerable uncertainty associated with them. A band deconvolution procedure was also employed in order to separate neighbouring band pairs, and the integrated areas obtained at the various temperatures were also analysed. However, it was observed that although integrated band areas gave much the same values for $\Delta H°$, they resulted in larger scattering in the van 't Hoff plots than the peak heights. The $\Delta H°(a-e)$ values obtained for TFCNCB were 3.3, 4.0 and 4.3 kJ mol^{-1}, with an average of 3.9 kJ mol^{-1} and an estimated uncertainty of 0.9 kJ mol^{-1}. Since the *a*-conformers of both TFCLCB and TFCNCB were not trapped in the matrix spectra (either in argon or in nitrogen), the hot nozzle method could not be employed to determine the enthalpy difference $\Delta H°$ in the vapour phase.

The variable temperature measurements reveal that the enthalpy differences $\Delta H°(a-e)$ of TFCLCB and TFCNCB are both equal within the error limits. As mentioned earlier, it is expected that the $\Delta H°$-values of the present molecules are quite similar to those of chloro-[2] and cyanocyclobutane,[5] since the two pairs of geminal fluoro substituents are converted into an identical configuration upon ring inversion. Qualitative estimations of the band intensities indicated that the conformational equilibria in chloro- and cyanocyclobutane were more displaced than in TFCLCB and TFCNCB, since the axial bands were more prominent in the latter. Earlier results obtained for chlorocyclobutane[2] and cyanocyclobutane[5] gave $\Delta H°(a-e)$-values equal to 5.7 and 4.8 kJ mol^{-1}, respectively, significantly higher than for the present com-

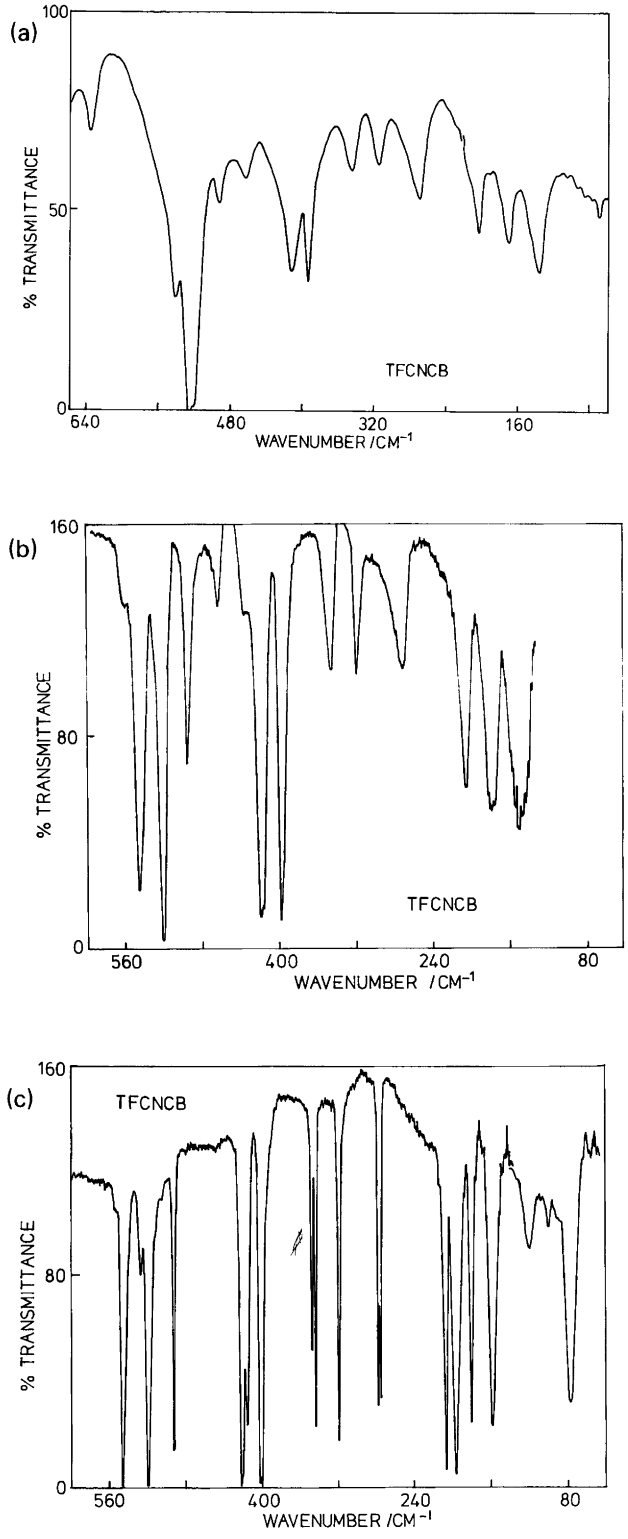

Fig. 12. Far-IR spectrum of TFCNCB, Mylar beamsplitters of thickness 3.5 and 12 μm: (a) dissolved in cyclohexane, (b) an amorphous solid at 80 K and (c) a crystalline solid at 80 K.

pounds. If two different halogens, competing for the favourable *e*-position, are attached to the same carbon, a much lower $\Delta H°$-value is expected between the conformers, as mentioned in the introduction. Thus, in 1-chloro-1-fluoro,[8] 1-chloro-1,2,2-trifluoro[8] and 1,1,2-trichloro-2,3,3-trifluorocyclobutane,[9] $\Delta H°$-values between 0.9 and 2.9 kJ mol^{-1} were found. Invariably, the more stable conformer in these three molecules had an equatorial F and an axial Cl substituent. Since $\Delta H°(a-e)$ was reported to be 4.5 kJ mol^{-1} in the liquid for fluorocyclobutane,[1] compared with 5.7 kJ mol^{-1} for chlorocyclobutane,[2] the preference for equatorial F in these three molecules may seem surprising, and indicates no simple additivity in the enthalpy terms.

Matrix isolation spectra were recorded with various purposes in mind. Since the bandwidths are generally much smaller in the matrix spectra than in the corresponding spectra recorded of the vapour and liquid, we expected more details in the matrix spectra and for bands of the two conformers, overlapping in the vapour and liquid states, to appear as resolved bands. However, the IR spectra obtained of TFCLCB and TFCNCB isolated in argon and nitrogen matrices at 13 K bore a somewhat disappointing resemblance to the spectra of the crystals, and only limited information of conformational interest could therefore be extracted from the matrix spectra. Annealing experiments, in which the matrix was heated to ca. 35 K, resulted in no significant intensity variations in the spectra except for some minor matrix effects, and when the gas mixtures, heated to elevated temperatures by a hot nozzle (e.g. 400, 500 and 600 K), were sprayed onto the cold window, the resulting spectra were again quite similar to those from the room-temperature gas deposits.

When a new closed-cycle cryostat with a Joule–Thomson stage, capable of giving 4.8 K on the window, became available in our laboratory, all the matrix experiments were repeated (with the nozzle temperature at ca. 300 K). Although the matrices deposited at this temperature were less transparent, giving rise to a strong background in the high-wavenumber region, the bands were slightly sharper than those obtained at 13 K. However, no axial bands were detected in any of the spectra. Together these observations imply that the high-energy conformer was never trapped in the matrices, but was converted into the more stable form as a result of the thermodynamic equilibrium.

Our expectation was that at this temperature (4.8 K) the unstable conformer would be trapped. Deposition was done very slowly at this temperature to ensure that the temperature of the window would not be raised. The behaviour on the 4.8 K window is surprising to us, as it strongly implies a very small barrier[16] of less than 1.5 or 2 kJ mol^{-1}. This is substantially lower than the values for the inversion barrier for similar compounds, which range from 2.7 to 4.7 kJ mol^{-1} and which have been obtained from a study of the low-frequency transitions. These values for the barrier for conversion from the axial to the equatorial conformer for the following monosubstituted cyclobutanes are (in kJ mol^{-1}) fluorocyclobutane,[1] 3.2;

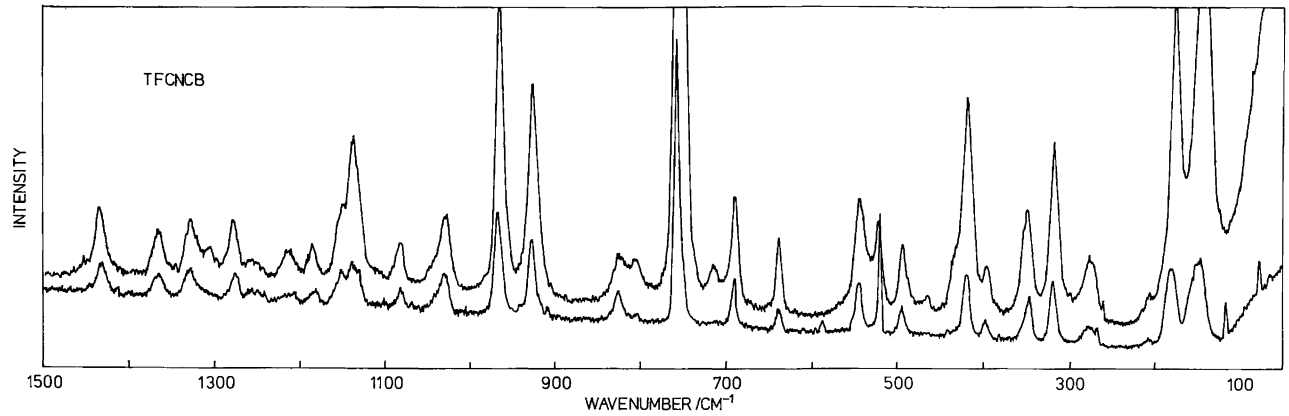

Fig. 13. Raman curves of TFCNCB below 1500 cm^{-1}: upper curve, liquid at 285 K, lower curve crystal at 80 K.

chlorocyclobutane,[3] 4.5; bromocyclobutane,[4] 3.3, ethynylcyclobutane,[7] 2.7 and methylcyclobutane,[7,17] 4.7.

In retrospective, this behaviour is perhaps not so surprizing, since the high-energy axial conformer in chloro-,[2] bromo-[2] and cyanocyclobutane,[5] as well as in 1-chloro-1-fluorocyclobutane[8] could never be trapped in a matrix at 14 K. In 1-chloro-1,2,2-trifluorocyclobutane,[8] however, the matrices contained both conformers, and when the original matrices of this compound deposited at 14 K were annealed to 36 K (argon) or 34 K (nitrogen) some bands increased and others decreased in intensity.[8] At higher nozzle temperatures the bands belonging to the high-energy conformer were enhanced. However, for this compound also the barrier was not sufficiently high to allow quantitative determination of the enthalpy difference $\Delta H°$ in the matrices. In 1,1,2-trichloro-2,3,3-trifluorocyclobutane[9] on the other hand, both conformers were effectively trapped both in argon and in nitrogen matrices, and quite accurate $\Delta H°$-values were observed in the matrices, suggesting that the barrier was higher that 7.5 kJ mol^{-1} for this compound.

Ab initio *calculations.* The *ab initio* values of 4–6 kJ mol^{-1} for the energy difference between the two conformers of TFCLCB compare reasonably with the value obtained for the liquid phase. The calculated puckering potential, Fig. 15, is also in accordance with our results from matrix isolation in the sense that our inability to trap the high-energy conformer at 4.8 K suggests a very low barrier to conformational interconversion. As to the calculated vibrational wavenumbers, they show a systematic deviation from the observations which is only to be expected, considering the numerous approximations involved. We refrain from commenting on the *ab initio* calculated structural parameters as they, not surprisingly, resemble those of related molecules in similar calculations.

Spectral interpretations. As is apparent from Table 1, approximately 12 IR and Raman bands of TFCLCB, all observed below 1400 cm^{-1}, vanished in the crystal

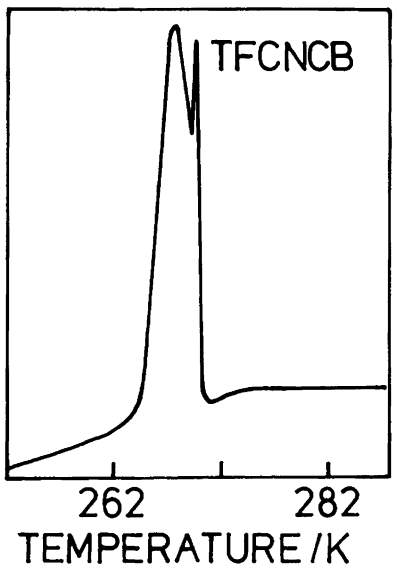

Fig. 14. Differential scanning calorimeter curves for TFCNCB, recorded in the heating cycle at a rate of 10 K min^{-1}.

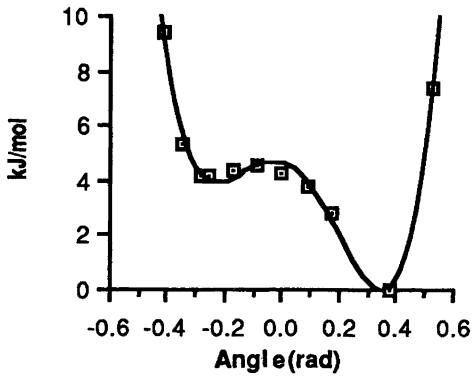

Fig. 15. Ab initio calculated potential to the ring inversion in TFCLCB, 3-21G* basis set.

spectra and were accordingly attributed to the high-energy Cl (*a*) conformer. The remaining bands of this conformer apparently coincide with those of the more stable conformer, meaning that a considerable number of *e*- and *a*-fundamentals overlap. This is expected in a compound for which the conformational equilibrium is highly displaced towards one side (equatorial). Only intense IR and Raman bands of the high-energy axial conformer could be detected in a mixture of the much more abundant equatorial conformer. Therefore, the assigned fundamentals in Table 1 are based upon the equatorial conformer, and fundamentals assigned to the axial conformer are marked with a prime.

The observed fundamentals are compared with those calculated from the normal coordinate analysis in Table 3. As is apparent, the agreement between the observed and calculated wavenumbers is satisfactory, considering that the scaling factors for 1-chloro-1-fluoro- and 1-chloro-1,2,2-trifluorocyclobutane[8] were directly transferred to TFCLCB. An exception is ν_{24} of the *a*-conformer observed at 408 cm^{-1} and calculated at 356 cm^{-1}. Alternatively, the *a*-bands at 408 cm^{-1} might be considered as a combination band and the 358 cm^{-1} band correlated with the calculated wavenumber at 356 cm^{-1}. Since the two molecules have no symmetry, the assignments cannot be supported by vapour-band contours or Raman polarization measurements.

In the spectra of TFCNCB eight bands were assigned to the high-energy conformer (Table 2). Since the conformational equilibrium is still more displaced towards the *e*-conformer in this molecule, the assignment of the *a*-fundamentals is quite uncertain. The force constant calculations for this molecule were based upon the *ab initio* force constants for TFCLCB modified with the force constants derived for cyanocyclobutane.[5,15] It can be seen from Table 4 that the assigned fundamentals of the *e*-conformer ν_6–ν_{13} are all too high compared with the calculated frequencies. Much better agreement could be achieved by introducing 1417 cm^{-1} as ν_6 and considering 1136 cm^{-1} as a combination mode. However, all the assigned fundamentals ν_6–ν_{13} had strong or medium intense Raman bands, and the suggested change was therefore not considered feasible.

A large number of observed bands in the spectra of both compounds were not assigned as fundamentals. They can in nearly all cases be considered as combination bands or overtones. Because of the large number of fundamentals in these molecules and the lack of symmetry no attempts were made to explain these bands, which can in many cases be done with several alternatives. However, nearly all the Raman bands of reasonable intensities have been attributed to fundamentals.

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References

1. Durig, J. R., Lee, M. J., Zhao, W. and Little, T. S. *Struct. Chem. 3* (1992) 329.
2. Gatial, A., Klæboe, P., Nielsen, C. J., Powell, D. L., Sülzle, D. and Kondow, A. J. *J. Raman Spectrosc. 20* (1989) 239.
3. Durig, J. R., Little, T. S. and Lee, M. J. *J. Raman Spectrosc. 20* (1989) 757.
4. Durig, J. R., Lee, M. J. and Little, T. S. *J. Raman Spectrosc. 21* (1990) 529.
5. Powell, D. L., Gatial, A., Klæboe, P., Nielsen, C. J., Kondow, A. J., Boettner, W. A. and Mulichak, A. M. *Acta Chem. Scand. 43* (1989) 441.
6. Dakkouri, M., Ruedel, K., Typke, V. and Caminati, W. *Acta Chem. Scand., Ser. A42* (1988) 519.
7. Durig, J. R., Geyer, T. J., Little, T. S. and Dakkouri, M. *J. Phys. Chem. 89* (1985) 4307.
8. Powell, D. L., Gatial, A., Klæboe, P., Nielsen, C. J. and Kondow, A. J. *J. Mol. Struct. 300* (1993) 209.
9. Gatial, A., Klæboe, P., Nielsen, C. J., Powell, D. L., Kondow, A. J. and Incavo, J. A. *J. Mol. Struct. 295* (1993) 73.
10. Harris, W. C. and Yang, D. B. *J. Mol. Struct. 18* (1973) 257.
11. Miller, F. A. and Harney, B. M. *Appl. Spectrosc. 24* (1970) 291.
12. Woldbak, T., Berkessel, A., Horn, A. and Klæboe, P. *Acta Chem. Scand., Ser. A36* (1982) 719.
13. Braathen, G. O., Gatial, A. and Klæboe, P. *J. Mol. Struct. 157* (1987) 73.
14. Gaussian 90, Revision I; Frisch, M. J., Head-Gordon, M., Trucks, G. W., Foresman, J. B., Schlegel, H. B., Raghavachari, K., Robb, M., Brinkley, J. S., Gonzales, C., Defrees, D. J., Fox, D. J., Whiteside, R. A., Seeger, R., Melius, C. F., Baker, J., Martin, R. L., Kahn, L. R., Stewart, J. J. P., Topiol, S. and Pople, J. A., Gaussian Inc., Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh PA (1990).
15. Woldbak, T., Nielsen, C. J. and Klæboe, P. *Spectrochim. Acta, Part. A41* (1985) 43.
16. Barnes, A. J. *J. Mol. Struct. 113* (1984) 443.
17. Kalasinsky, V. F., Harris, W. C., Holtzclaw, P. W., Little, T. S., Geyer, T. J. and Durig, J. R. *J. Raman Spectrosc. 18* (1987) 581.

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