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Spectroscopic Conformational Analysis of Some Monohalogenated *Cyclo*hexanes

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The vibrational spectra of monohalogenated *cyclo*hexanes in the liquid and solid states have been investigated.

In the liquid state of monochloro- and monobromo-*cyclo*hexane both the *e*- and the *a*-conformation are present, the *e*-conformation preponderating in both compounds. The same dynamic equilibrium between the two conformations of monochloro*cyclo*hexane was observed in the rotating, cubic modification. No cubic modification was found for the monobromo-compound. In the anisotropic modification (at −150° C) only the *e*-conformation of the two compounds could be detected.

Investigation of the spectra of monofluoro*cyclo*hexane in the liquid, cubic (rotating) and anisotropic modification revealed the presence of only one conformation.

The stereochemistry of halogen substituted *cyclo*hexanes has been studied in considerable detail by Hassel and co-workers [1] using X-ray and electron diffraction methods and in some cases dipole moment measurements. As a result of the investigation of *cyclo*hexane Hassel [2] pointed out that for the majority of the substituted *cyclo*hexanes two different conformations are possible through the conversion of the carbon ring. In the vapour the relative amounts of the two conformations present at equilibrium are to a large extent determined by steric factors. In the solid state only one of the two possible conformations has been observed.

The electron diffraction method will in most cases not be sensitive enough to detect a small percentage of one conformation in an equilibrium. The method is furthermore not suited for investigation of the liquid phase.

It was hoped, however, that the infrared spectrophotometric method would be more sensitive to small amounts of a second conformation. The method might also be valuable in elucidating the structure of some of the more complicated halogen substituted *cyclo*hexanes.

A great advantage of the infrared method is that it is equally suited for the solid, liquid and even for the vapour phase of the lower boiling compounds. Since the two conformations of monohalogeno derivatives of *cyclo*-

hexane represent two different molecular species, they will have two different sets of vibrational frequencies. Some of the corresponding infrared bands, at least in the lower frequency region, should be so strongly influenced by the different directions of the halogen substituent that they should be resolved by an infrared spectrophotometer. Provided that only one conformation is present in the solid state it should be possible by noting the disappearance of a set of bands on going from the liquid to the solid state to assign some of the bands to one or another of the two conformations. The more complicated problem to decide which of the two conformations is present in the solid state may be solved either by an X-ray study or in more special cases by direct assignment of some of the bands to each of the two conformations. This assignment is greatly facilitated if polarization data from the Raman spectrum are available, or, as will be discussed in a forthcoming paper [3], if it is possible to displace the conformational equilibrium by changing the solvent.

As an introduction to the spectroscopic study of the stereochemistry of halogen substituted *cyclo*hexanes a discussion of the infrared and Raman spectra of monochloro- and monobromo-*cyclo*hexane and of the infrared spectrum of monofluoro*cyclo*hexane is presented in this paper. In a subsequent paper [3] the spectra of some 1,2-dihalogen substituted *cyclo*hexanes will be dealt with.

An electron diffraction investigation of the vapour of monochloro*cyclo*hexane published in 1943 by Hassel and Viervoll [4] has shown that the *e*-conformation must be present in a concentration considerable greater than the *a*-conformation.

More recently Larnaudie [5] in a study of the infrared spectra of the monohalogenated *cyclo*hexanes concluded from a consideration of the band envelopes of the vapour spectra that both conformations of the iodo-, bromo-, chloro-, and probably also of the fluoro-compound were present in the liquid phase. It is obvious, however, that the band envelopes are not very sensitive to the structure of these molecules of low symmetry (C_s), and the interpretation given by Larnaudie cannot be regarded as conclusive.

It has been known for several years that some simple derivatives of *cyclo*hexane exhibit molecular rotation in the crystals just below the melting point. This phenomenon has been shown both for *cyclo*hexane itself and for monochloro*cyclo*hexane [6]. Usually organic compounds which exhibit rotation below the melting point crystallize in the cubic system. This rotation can, however, not continue down to the absolute zero of temperature. The crystals must consequently undergo a transition into a non-rotating, generally anisotropic modification. This gives us the possibility of learning, by means of polarized light, whether the crystals are in a rotating or a non-rotating state.

The true nature of molecular rotation in the crystal lattice is not very well understood, but it will be shown in this paper that the rotation in the cubic modification permits the free interconversion between the two conformations.

EXPERIMENTAL

The *cyclo*hexane derivatives were synthesized using well known methods and their purity checked by the refractive indices.

Table 1. Raman and infrared spectra of monochlorocyclohexane.

Raman spectrum liquid (20° C)			Infrared spectra liquid (25° C)		rot. cubic modif. (−60° C)	solid modif. (−150° C)
$\Delta\nu$ cm^{-1}	I	ϱ	ν cm^{-1}	I	ν cm^{-1}	ν cm^{-1}
1 461	1		1 462	1	1 462	1 462
1 446	6	0.72	1 450	10	1 449	1 450
1 429	0		1 434	1	1 434	1 438
1 349	2	0.61	1 352	3	1 352	1 352
1 338	2		1 339	4	1 339	1 337
			1 325	1	1 325	1 325
1 302	1	0.80	1 301	0	1 300	1 302
1 270	3	0.69	1 267	10	1 269	1 270
1 261	4		1 262	10	1 261	1 259
1 216	1	0.78	1 217	8	1 218	1 219
1 184	1	0.85	1 186	0	1 186	1 187
1 132	1	0.37	1 132	1	1 134	1 134
			1 098	3	1 098	
			1 088	0	1 088	1 089
1 074	1	0.85				
1 051	1	0.88	1 050	0	1 052	1 056
1 028	4	0.65	1 030	2	1 029	1 031, 1 026
			1 014	4	1 016	
993	3	0.41	993	8	994	994
921	0	p	920	1	920	920
889	0	0.73	888	8	888	888
868	0	p	867	4	869	
			858	5	859	
852	2	0.25	852	2	852	850
818	3	0.19	816	8	817	817
807	3	0.18	806	3	807	
732	8	0.19	728	9 b	726	726
686	2	0.15	683	5	684	
586	0	p				
559	2	0.15	557	7		
512	1	0.18	512	5		
471	0	p	471	3	not recorded	
435	1	0.14	434	2		
382	0	p				
339	10 b	0.19	340	6 b		
			298			
258	1	0.67		2		
199	0	p				

The infrared spectra were recorded with a Perkin-Elmer Model 21 double beam spectrophotometer equipped with sodium chloride and caesium bromide prisms. A cell similar to the one described by Lord *et al.*[7], was used and only minor alterations introduced in order to record the spectra at low temperatures. Teflon spacers were, however, found to be more efficient than the conventional metal spacers to prevent leakage. One welding point of the thermocouple was placed as close as possible to the cell windows and a rough estimate of the temperature gradient between this spot and the sample was made. Before running the spectra the solids were inspected by placing the cell in a light beam between two opposed polaroid films.

The Raman spectra were recorded with a three-prism f : 3, Steinheil spectrograph. The source unit consisted of eight 450 watts mercury lamps surrounded by a cylindrical

Table 2. Raman and infrared spectra of monobromocyclohexane.

Raman spectrum liquid (20° C) $\Delta\nu$ cm^{-1}	I	ϱ	Infrared spectra liquid (25° C) ν cm^{-1}	I	solid modif. (−150° C) ν cm^{-1}
1 446	4	0.84	1 448	10	1 444
1 349	3	0.62	1 346	2	1 346 ?
1 336	1		1 334	6	1 332
1 301	1		1 297	1	1 296
1 273	1				
1 257	5	0.52	1 252	10	1 256
1 195	4	0.53	1 189	10	1 192
			1 139	0	1 138
1 117	2		1 116	6	1 120
1 088	1		1 086	4	1 086 ?
1 061	2				
1 052	2				
1 029	4	0.90	1 026	1	1 026
			1 009	5	
990	5	0.45	987	9	989
			919	1	919
888	1		885	8	886
865	1		862	2	
849	4	0.30	850	6	846
809	6 b	0.54	811 804	8 4	810
688	8	0.40	685	9	684
659	3	0.28	658	6	
503	4 b	0.23	503	5	
460	3	0.35	457	5	
			436	1	
			428	2	
411	2				
371	2				not recorded
298	2		299	1	
262	10	0.30			
243	2				
221	2				

metal jacket the inner surface of which was coated with magnesium oxide [8]. The same source unit, with the addition of a set of parallel baffles inside the circle of mercury lamps, was used in order to obtain polarization data by means of the two-exposure method by Crawford and Horwitz [9].

EXPERIMENTAL RESULTS

The infrared and Raman data for the monochloro- and the monobromo-*cyclo*hexane in the liquid and solid states are reproduced in Tables 1 and 2. The frequencies for the Raman spectra of these compounds are in reasonably good agreement with those reported by Kohlrausch [10]. The most significant difference is found in the Raman spectrum of the chloro compound. We have found two polarized lines of about equal intensity at 807 and 818 cm^{-1}. Kohlrausch observed only one line. The polarization data of Tables 1 and 2 represent the average of four plates and should be more reliable than the results from the rather incomplete investigation by Canals [11].

Table 3. Infrared spectra of monofluorocyclohexane.

liquid (25° C)		rot. cubic modif. (−25° C)	solid modif. (−150° C)
ν cm^{-1}	I	ν cm^{-1}	ν cm^{-1}
			1 495
			1 471
1 456	10	1 454	1 454
			1 394
1 370	10	1 370	1 369
1 350	5	1 350	1 351
1 344	5	1 343	1 343
1 332	5	1 331	1 330
			1 317
			1 297
1 263	4	1 263	1 263
1 247	1	1 249	1 252
1 195	2	1 196	1 194
1 162	6	1 163	1 163
			1 145
1 130	8	1 131	1 129
1 098	4	1 099	1 098
		1 078	1 079
1 050	10	1 050	1 048
1 034	9	1 034	1 034
1 020	10	1 018	1 018
962	10	960	958
942	10	938	939
			926
894	8	896	896
869	3	870	869
847	6	848	844
834	7	834	833
794	6	795	795
		732	733
719	1	719	717
677	0	676	676
662	2	662	660

It is very interesting to note that all of the bands observed in the liquid state of monochloro*cyclo*hexane (Table 1) are also found in the cubic, semi-solid modification. A set of bands has disappeared, however, from the spectrum of the solid, anisotropic modification at —150° C.

For the monobromo-compound only *one* crystalline modification has been found [6]. Inspection in polarized light revealed that the crystals were anisotropic. A comparison of the infrared bands of the two states (Table 2) shows that a set of bands disappeared on going from the liquid to the solid state. Only by very slow cooling and crystallization of the bromo compound could these bands be eliminated.

The infrared data for the monofluoro*cyclo*hexane in the liquid state are in good agreement with a spectrum obtained by Bak [12]. The data for the liquid state and for the two crystalline modifications are given in Table 3. It will be seen that in this case all the bands observed for the liquid state are present in the semi-solid, cubic as well as in the solid, anisotropic modification. The

infrared spectrum of the anisotropic modification was repeatedly investigated with the same result.

The infrared spectra of solutions of the monochloro- and monobromo-compound in different solvents of high and low dielectric constant (nitromethane - *cyclo*hexane) did not reveal any change in the conformational equilibrium, judging from the relative absorbancy values of the bands.

DISCUSSION

The discussion will mainly be concerned with monochloro*cyclo*hexane as this compound exhibits all of the special features of substituted *cyclo*hexanes: Both conformations are present in the liquid state; two solid modifications are found, one cubic, rotating, where both conformations are observed, and one anisotropic, non-rotating, where only one of the two conformations can be present.

The monochloro*cyclo*hexane molecule possesses $3 \times 18 - 6 = 48$ normal modes of vibration which are all active both in the infrared and the Raman spectra. A more detailed consideration indicates that the molecule would be expected to have at most 6 polarized Raman lines below 700 cm^{-1}: 4 ring frequencies, 1 C—Cl stretching and 1 C—Cl bending frequency. The Raman spectrum of liquid monochloro*cyclo*hexane (Table 1) shows, however, a great number of polarized, strong Raman lines in the lower frequency region, 16 below 1 000 cm^{-1} and 9 below 700 cm^{-1}. Already this behaviour indicates strongly that both conformations must be present in appreciable concentrations in the liquid state of monochloro*cyclo*hexane. This assumption is confirmed by the observation that several bands of high intensity in the spectrum of the liquid are lacking from the spectrum of the solid at —150° C. As only one conformation can be present in the true solid state, this behaviour points unequivocally to an equilibrium between the two conformations in the liquid state. Only with molecules of high symmetry, where forbidden bands are observed in the liquid state owing to the breaking-down of the selection rules, may some of these bands disappear on going to the solid state.

The Raman spectrum of liquid monobromo*cyclo*hexane (Table 2) does not as clearly indicate the presence of two conformations as was the case with the chloro compound. Only 5 lines below 700 cm^{-1} can unambigously be identified as polarized. The intensity of the other lines is too low to permit observation of the polarization ratio. A consideration of the total number of frequencies, 15 in all, observed below 700 cm^{-1} in the Raman and infrared spectra indicates, however, that both conformations are probably present in the liquid state as about 9 frequencies only would be expected for monobromo*cyclo*hexane. A comparison of the liquid and solid state infrared spectra of monobromo*cyclo*hexane shows, furthermore, that at least 4 bands of medium intensity are lacking from the solid state spectrum. Unfortunately, the solid state spectrum has only been run in the sodium chloride region, but it is quite probable that a study of the spectrum below 650 cm^{-1} would reveal the absence of other bands. At any rate the presence of both conformations in the liquid state is clearly revealed.

For monofluoro*cyclo*hexane all of the infrared bands present in the liquid persisted in both the cubic and in the anisotropic modification. It seems thus as if only *one* conformation can be detected in the liquid state of the monofluoro compound.

ASSIGNMENTS

It would be of great help for the infrared determination of the structure of polyhalogenated *cyclo*hexanes if some bands could be assigned to definite groupings within the molecules. Attention should especially be paid to the effect of *a*- and *e*-substituents on the position and intensity of the bands.

The infrared spectra of the monohalogenated *cyclo*hexanes would be expected to have at least 3 comparatively strong bands in which the polar carbon-halogen linkage participates to a large extent in the vibration *. The stretching of the carbon-halogen bond, a totally symmetrical vibration and consequently polarized in Raman, would be expected to show up strongly in both the infrared and the Raman spectra. Of the two vibrations connected with the bending of the carbon-halogen bond, one should give a polarized, the other an unpolarized Raman line.

Kohlrausch [10] identifies the C—Cl stretching vibration of monochloro*cyclo*hexane with the very strong, polarized Raman line at 732 cm^{-1}. Kohlrausch did not, however, consider the possibility of two conformations. As the C—Cl stretching frequency is usually found around 700 cm^{-1}, it is reasonable to assign the polarized Raman line at 686 cm^{-1} to the C—Cl stretching frequency of the other conformation. This corresponds well with the observation that the 732 cm^{-1} band persists in the infrared spectrum of the solid, whereas the 686 cm^{-1} band is absent.

The polarized and very strong Raman line at 339 cm^{-1} in the spectrum of the chloro compound is obviously the C—Cl bending vibration. It is somewhat surprising that the corresponding band for the other conformation has not been identified. Probably this band is located in the region below 200 cm^{-1} which is obscured by the exciting Raman lines. It is also possible that the line is covered by the broad 339 cm^{-1} line.

The pair of lines at 807 and 818 cm^{-1}, both equally strongly polarized in the Raman spectrum of monochloro*cyclo*hexane, are probably the symmetrical ring stretching frequencies of the two conformations, corresponding to the line at 802 cm^{-1} in *cyclo*hexane [13].

The bands at 1 014 and 1 098 cm^{-1}, lacking in the spectrum of solid monochloro*cyclo*hexane may be ascribed to the methine C—H group, or possibly to a ring stretching frequency. This question will be discussed more completely in the forthcoming paper on dihalogenated *cyclo*hexanes.

The assignment of the bands in the spectra of monobromo*cyclo*hexane will be mentioned in a few words. The polarized Raman lines at 688 and 659 cm^{-1} are obviously the C—Br stretching vibrations of the two conformations. The very strong and polarized Raman line at 262 cm^{-1} is the symmetrical

* It should be pointed out that the term "polar" here has a real physical signification and should not be mistaken for the old designation used in the *cyclo*hexane stereochemistry instead of an axial -*a*-substituent.

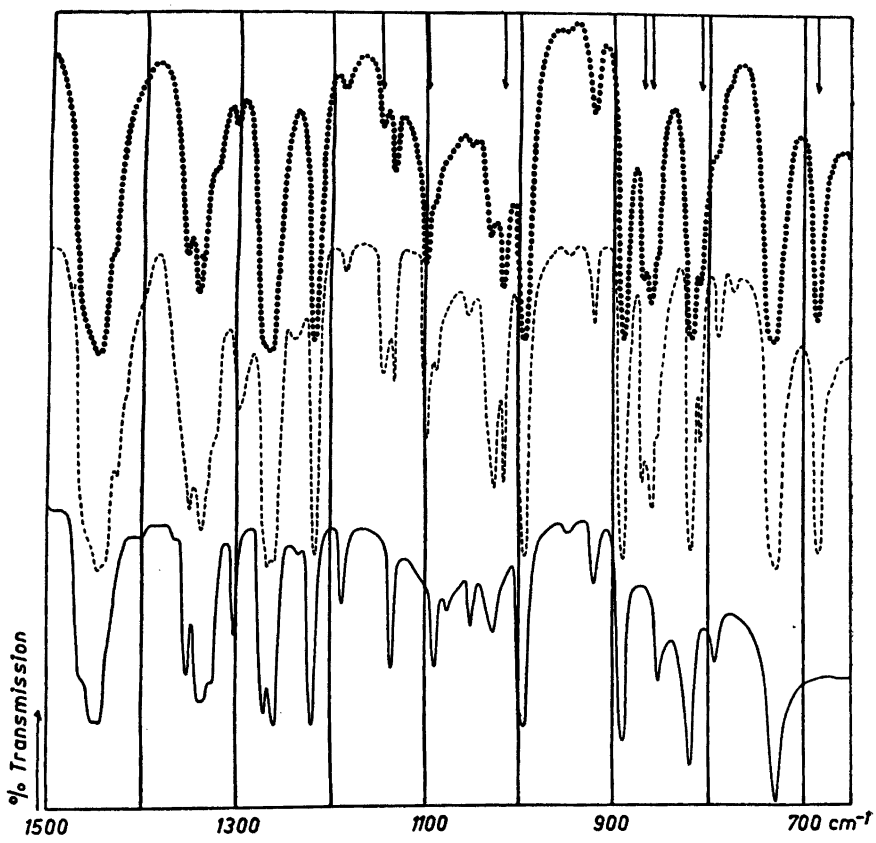

Fig. 1. Infrared spectra of monochlorocyclohexane.
..... *liquid at +20° C*
– – – – – *cubic, rotational modification at −60° C*
——— *solid, anisotropic modification at −150° C*

The bands that are assigned to the a-conformation, are indicated by arrows.

deformation vibration of the C—Br linkage of one of the two conformations. Again it is not quite clear where the C—Br bending frequency of the other conformation is located. The symmetrical ring stretching frequency, at 802 cm^{-1} in *cyclo*hexane, is probably found at 809 cm^{-1} in monobromo*cyclo*hexane. A close inspection of the Raman spectrum reveals that the 809 cm^{-1} band is a doublet. Seemingly the symmetrical ring stretching frequency of the halogeno compounds is not very sensitive to the geometrical direction of the substituent.

The problem of deciding which of the two conformations is present in the solid state of monochloro- and monobromo-*cyclo*hexane is best solved by considering the relative positions of the carbon-halogen stretching frequencies. As will be evident from the forthcoming paper on dihalogenated *cyclo*hexanes,

there are strong indications that the carbon-halogen stretching vibration is of higher frequency in the *e*-conformation than in the *a*-conformation. Consequently, the C—Cl stretching band of monochloro*cyclo*hexane at 728 cm^{-1} should be assigned to the *e*-conformation. The observed ratio of the intensities of the 728 cm^{-1} and the 683 cm^{-1} band is as 2 to 1 in the liquid infrared and somewhat higher in the Raman spectrum; this is in accordance with the general trend of the intensity ratios of other pair of bands in the spectra. Qualitatively, the higher intensity of the *e*-band is in good agreement with the observation by Hassel and Viervoll [2] that only the *e*-conformation could be detected in the vapours by the electron diffraction method.

Correspondingly, of the two C—Br stretching frequencies of monobromo-*cyclo*hexane, the 685 cm^{-1} band should be assigned to the *e*-conformation and the 658 cm^{-1} band to the *a*-conformation.

These assignments make it possible to identify the conformation in the solid. Tables 1 and 2 show that of the carbon-halogen stretching frequencies it is the *a*-bands, 683 cm^{-1} in the monochloro- and 658 cm^{-1} in the monobromo-compound, that disappear in the solid state spectra. Consequently, the *e*-conformations are energetically preferred in the lattice of the anisotropic modifications of both the monochloro- and the monobromo-*cyclo*hexane. A conclusion regarding the conformation present in crystalline monofluoro*cyclo*-hexane cannot be reached at the present time.

ROTATIONAL, SEMISOLID STATE

The observed close similarity of the spectra of monochloro*cyclo*hexane in the liquid state and in the semi-solid, cubic modification is quite interesting but not surprising. The disappearance of a set of bands on going to the solid, anisotropic modification provides a clear evidence for the presence of two conformations both in the liquid and in the cubic modification. As the energy barrier of the conversion of the carbon ring is very low and considering the easy transition of one conformation into the other at the transition-point, a static equilibrium can be excluded. The conclusion must be that the molecular rotation permits an unhindered interconversion of the two conformations in the cubic lattice. Furthermore it must be assumed that the dynamic equilibrium ratio between the two conformations is approximately the same in the liquid and in the rotational, cubic state of monochloro*cyclo*hexane.

Monofluoro*cyclo*hexane also exhibits molecular rotation in the cubic lattice. In this case, however, all spectra of the solid states at any temperature down to —150° C were identical with that of the liquid compound, although a transition from the cubic to an anisotropic modification at a higher temperature was ascertained by inspection in polarized light. This leads to the conclusion that only *one* conformation of the monofluoro*cyclo*hexane can be identified in the solid as well as in the cubic, semi-solid and liquid states of the compound. The physical explanation of this behaviour may possibly involve a stabilizing effect by intramolecular C——H- - -F bonding due to the strong electronegativity of the fluorine atom. The finding that only one conformation prevails, even when steric interactions does not exclude the other conformation, is not unique [14].

The spectrum of the solid monobromo*cyclo*hexane is not changed through the temperature range from just below the melting point to —150° C. This is in full accordance with the lack of a cubic, rotating state for this compound.

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