ROTATIONAL ISOMERISM IN DICHLOROACETYL HALIDES

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by

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ABSTRACT

Infrared and Raman spectra have been measured for $CHCl_2COF$, $CHCl_2COCl$ and $CHCl_2COBr$ and it is concluded that two molecular forms exist in the vapour and liquid phases, of which the more polar form is present in excess in the solid state. The enthalpy difference between these isomers has been measured for $CHCl_2COCl$ and $CHCl_2COBr$ in the vapour phase and found to be small. Vibrational assignments are made and the nature of the stable conformations is discussed with the help of an analysis, based on a Urey-Bradley potential function.

CONTENTS

Page

EXPERIMENTAL

RESULTS AND DISCUSSION

APPENDICES

Introduction

Many papers have been published on the subject of infrared spectroscopic studies of rotational isomerism. S.Mizushima who is perhaps the greatest authority on this topic, has, with other workers, made such a study for dichloroacetyl chloride(1). They concluded that two rotational isomers coexist in the vapour and liquid phases, but only the more polar form remains in the solid state. A comparison of observed and calculated frequencies suggested that the less polar form of the molecule has the oxygen atom in the cis-position with respect to the hydrogen atom, and the use of the well-known product rule, together with the results of electron diffraction experiments indicated that the more polar conformation is obtained from the less polar one by an internal rotation of approximately 90°.

The present work has used similar techniques to examine the series $CHCl_2COF$, $CHCl_2COCl$ and $CHCl_2COBr$ in order to see if the experimental data for all three molecules may be interpreted in the above manner.

EXPERIMENTAL

The three compounds were prepared as follows; all samples being fractionally distilled two or three times before use:

a) $CHCl_2COF$ (b.p. 70 - 72°C; lit: 71-72°C (2))
by refluxing dichloroacetyl chloride and antimony trifluoride.

b) $CHCl_2COCl$ (b.p. 108°C; lit: 107-107.5°C (1))
by reaction of dichloroacetic acid and excess thionyl chloride.

c) $CHCl_2COBr$ (b.p. 125-128°C; lit: 125-129°C (3))
by reaction of the acid with phosphorus tribromide.

Infrared spectra were recorded with a Grubb-Parsons GS2A spectrometer in the range 400 - 4000 cm^{-1}. and a Perkin-Elmer '225' instrument from 200 - 400 cm^{-1}. In the high frequency range the pure liquids were run as liquid films between KBr discs and in the low frequency range between polythene discs. Dilute solution spectra were obtained with a matched pair of liquid cells and solvents varying from non-polar carbon tetrachloride and chloroform to more polar acetone and acetonitrile. A standard 10 cm. path length gas cell was used for vapour spectra, KBr windows being attached with a Teflon adhesive (4).

Many attempts were made to reduce the solid spectra of the compounds to those due to one conformer only, but all were unsuccessful

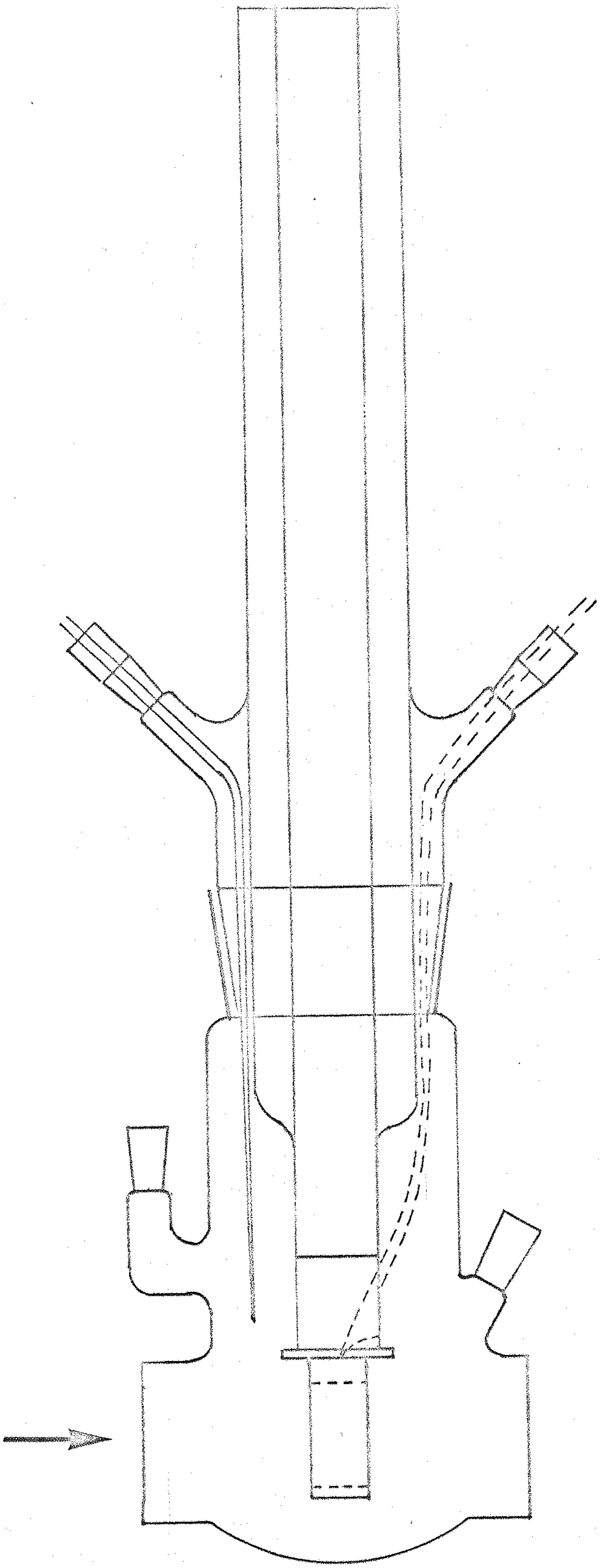


Fig. 1. The low-temperature cell.

despite the use of the following techniques:-

a) Formation of the solid sample either by cooling a liquid film or by directing vapour onto a cooled KBr disc.

b) Once formed, repeated warming of the solid to its melting point and recooling.

c) Changing the coolant from liquid nitrogen to various liquid nitrogen slushes.

The low-temperature cell used for this work is shown diagrammatically in Fig.1.

The Raman spectra of the pure liquids were measured with a Carey Raman spectrometer, equipped with a helium-neon laser.

Vibrational Analysis

It would seem necessary at this point to give some justification for the use of a Urey-Bradley potential function for this work, and in fact for the inclusion of a vibrational analysis.

A molecule containing N atoms cannot exhibit more than 3N-6 fundamental vibrational frequencies. However, in the case of the substituted acetyl halides, as for many other molecules, considerably more than 3N-6 absorption bands appear in the infrared and Raman spectra of the molecules, due to the coexistence of two stable conformations of the molecules. In solution the intensities of bands due to the more polar of these conformations increase with respect to those due to the less polar form, with increasing polarity of the solvent, and by comparing solution spectra and solid spectra, where the more stable rotamer predominates, it is possible to assign a set of absorption bands to each isomer. A vibrational analysis was included in the hope that by comparing these observed frequencies with those calculated for different conformations of the molecule it would be possible to draw conclusions as to the nature of the two stable conformations.

The advantages of the Urey-Bradley field are probably best shown by a comparison with the so-called General Force Field. If we define 3N-6 internal coordinates R_i, $i = 1$ to 3N-6, in order to describe small vibrations of the molecule, then the total potential energy of the molecule as a function of these coordinates may always be expanded in a Taylor series about the equilibrium configuration e(5):

$$V = V_e + \sum_i \left(\frac{\partial V}{\partial R_i}\right)_e R_i + \frac{1}{2} \sum_i \sum_j \left(\frac{\partial^2 V}{\partial R_i \partial R_j}\right)_e R_i R_j$$

$$+ \text{(terms in } R^3 \text{ and higher powers)}$$

V_e is trivial since it defines the zero of the energy scale and the second term is zero since derivatives are taken at the equilibrium configuration. Terms in R of order higher than R^2 are comparatively small, so that the potential function reduces to:

$$V = \frac{1}{2} \sum_i \sum_j F_{ij} R_i R_j$$

where the harmonic force constants F_{ij} are defined as

$$F_{ij} = \left(\frac{\partial^2 V}{\partial R_i \partial R_j}\right)_e \equiv \left(\frac{\partial^2 V}{\partial R_j \, \partial R_i}\right)_e$$

The main disadvantage of this function is immediately apparent, for in the case of the substituted acetyl halides, where one requires 15 internal coordinates to describe the system, the number of force constants required will be very large. It is possible to reduce the number in some cases by using the symmetry of the molecule and by equating many force constants with zero; but since the interactions between coordinates are difficult to visualise this is not easy.

The Urey-Bradley potential function takes the form:

$$\begin{aligned} V = & \sum_i \left[K_i' r_i (\Delta r_i) + \tfrac{1}{2} K_i (\Delta r_i)^2 \right] \\ & + \sum_i \left[H_i' r_i \alpha^2 (\Delta \alpha_i) + \tfrac{1}{2} H_i \; r_{i\alpha}^2 (\Delta \alpha_i)^2 \right] \\ & + \sum_i \left[F_i' q_{ij} (\Delta q_i) + \tfrac{1}{2} F_i (\Delta q_i)^2 \right] \end{aligned}$$

where Δr_i, $\Delta \alpha_i$ and Δq_i represent a change in bond length, bond angle, and the distance between non-bonded atoms, respectively, and the values r_i, $r_{i\alpha}$ and q_{ij} are equilibrium distances inserted to reduce all force constants to the same dimension.

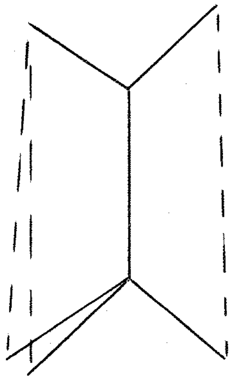
Here, unlike the General Force Field, there are no quadratic cross terms to take into account, for they are implicit in the interactions between non-bonded atoms. The actual physical meaning of the Urey-Bradley force constants is therefore far more readily visualised.

The main advantage is seen in the number of force constants, which may be made even smaller by the conventional assumption that $F_i' = -\frac{1}{10} F_i$ (which has been shown to be reasonable in many cases (6)).

Linear terms are included in the function because the changes Δr_i, $\Delta \alpha_i$ and Δq_i are obviously not independent. This redundancy is removed by expressing the Δq_i in terms of Δr_i and $\Delta \alpha_i$. The linear terms in the new equation can then be removed, since the partial derivatives $\frac{\partial V}{\partial r_i}$ and $\frac{\partial V}{\partial \alpha_i}$ may be equated to zero.

The general validity of the function to this type of molecule has been demonstrated and force constants, which are readily available in the literature, have been shown to be transferable (6,7).

The computer programs used for the analysis are due to J.H. Schachtschneider (Shell Development Company technical report). Brief details are given in Appendix 1. All computation was done on an I.C.T. 1907 machine. Initial results have been obtained assuming only interactions between nearest and next-nearest neighbour atoms following the procedure of previous workers. The vibrational potential energy is therefore assumed to be constant and independent of the azimuthal angle of internal rotation, and the variation of the calculated frequencies with azimuthal angle is purely a result of the change in the kinetic energy G matrix (see Appendix 1). This would seem to be a poor representation of a system in which the most important interactions are across the molecule (cis interactions) and it must be stressed that a comparison of frequencies calculated on this basis with those observed can only give an indication as to the probable nature of the stable conformations.



Tables 1 and 2 indicate the various parameters used in the analyses of $CHCl_2COF$ and $CHCl_2COBr$ (all H force constants are scaled by the C-C bond distance). The parameters used for $CHCl_2COCl$ are identical to those of Mizushima et al (1), and the agreement with their results is good.

Enthalpy Difference Measurements

The enthalpy difference between the stable conformations in the vapour phase has been measured for $CHCl_2COCl$ and $CHCl_2COBr$. The method involves monitoring the change in intensity of infrared absorption bands unique to each conformer with increasing temperature (8).

Consider a sample of thickness t absorbing radiation at a particular frequency. Let the intensity of the incident radiation be I_o and that of the transmitted radiation be I. Then, by the

TABLE 1.

Force constants and molecular parameters for $CHCl_2COF$

Force constants (mdyn/Å)		Bond length(Å)	Bond angle
K(C–C) = 2·80	F(Cl···H) = 0·80	r (C – H) = 1·09	α(F – C – O) = 125°
K(C–H) = 3·90	F(Cl···Cl) = 0·65	r (C – C) = 1·54	α(F – CO – L) = 110°
K(C–Cl) = 1·75	F(Cl···C) = 0·60	r (C – Cl) = 1·76	α(O – C – C) = 125°
K(C–F) = 4·00	F(C····H) = 0·40	r (C – O) = 1·22	all other angles = 109° 28'
K(C–O) = 11·00	F(F····O) = 1·60	r (C – F) = 1·37	
H(H–C–Cl) = 0·04	F(O····C) = 0·40		
H(Cl–C–Cl) = 0·13	F(F····C) = 1·30		
H(F–C–O) = 0·24	$F' = -\frac{1}{10}F$		
H(C–CO–F) = 0·13	K = 0·1		
H(C–C–O) = 0·32			
H(H–C–C) = 0·15			
H(C–C–Cl) = 0·23			

TABLE 2.

Force constants and molecular parameters for $CHCl_2COBr$

Force constants (mdyn/Å)		Bond length(Å)	Bond angle
K(C-C) = 2·80	F(Cl···H) = 0·80	r(C - H) = 1·09	α(Br - C - O) = 125°
K(C-H) = 3·90	F(Cl···Cl) = 0·65	r(C - C) = 1·54	α(Br - CO - C) = 110°
K(C-Cl) = 1·75	F(Cl···C) = 0·60	r(C - Cl) = 1·76	α(O - C - C) = 125°
K(C-Br) = 1·50	F(C····H) = 0·40	r(C - O) = 1·22	all other angles
K(C-O) = 11·00	F(Br···O) = 0·65	r(C - Br) = 2·00	= 109° 28'
H(H-C-Cl) = 0·04	F(O····C) = 0·40		
H(Cl-C-Cl) = 0·13	F(Br···C) = 0·70		
H(Br-C-O) = 0·40	$F' = -\frac{1}{10}F$		
H(C-CO-Br) = 0·13	K = 0·1		
H(C-C-O) = 0·32			
H(H-C-C) = 0·15			
H(C-C-Cl) = 0·23			

Beer-Lambert Law:

$$\ln\left(\frac{I_o}{I}\right) = -\varepsilon N t$$

where ε is the molecular absorption coefficient for the particular band being studied and N is the number of molecules per cc. in the infrared beam. Now consider the case of the substituted acetyl halides in which the molecules are able to rotate about the carbon-carbon bond. For an absorption band due to the more polar isomer we have

$$\ln\left(\frac{I_o}{I}\right)_m = -\varepsilon_m N_m t$$

(where m denotes the more polar conformation)

while for a band due to the less polar form

$$\ln\left(\frac{I_o}{I}\right)_\ell = -\varepsilon_\ell N_\ell t$$

Therefore
$$\frac{\ln\left(\frac{I_o}{I}\right)_\ell}{\ln\left(\frac{I_o}{I}\right)_m} = \frac{\varepsilon_\ell N_\ell}{\varepsilon_m N_m}$$

If the bands chosen are due to the same vibrational mode occurring in different conformations of the molecule, then, by making the assumption that the absorption coefficients of the two isomers are equal, i.e. that $\varepsilon_\ell = \varepsilon_m$, we have

$$\frac{\ln\left(\frac{I_o}{I}\right)_\ell}{\ln\left(\frac{I_o}{I}\right)_m} = \frac{N_\ell}{N_m}.$$

For a sample at rotational equilibrium the equilibrium constant $K = \frac{N_\ell}{N_m}$ and by the Van't Hoff equation

$$K = Be^{-\frac{\Delta H}{RT}}$$

Thus

$$\frac{\ell n\left(\frac{I_o}{I}\right)_\ell}{\ell n\left(\frac{I_o}{I}\right)_m} = Be^{-\Delta H/RT}$$

where ΔH is the enthalpy difference between the more polar and less polar forms, and B is a constant. Measurement of the relative optical densities of the two bands allows calculation of ΔH.

Since a sample absorbs radiation over a frequency interval, it is necessary to determine the integrated optical density A rather than the optical density at a particular frequency (9):

$$A = \int \ell n\left(\frac{I_o}{I}\right) d\nu$$

the integration being taken over the frequency interval of the absorption band.

The relevant equation thus becomes

$$\ell n\left(\frac{A_\ell}{A_m}\right) = -\frac{\Delta H}{RT}$$

Obviously for an accurate determination of the relative absorbances the two bands considered must be completely resolved. No suitably resolved peaks appear in the vapour spectrum of $CHCl_2COF$ and no ΔH determination has been made for the compound.

A standard gas cell is used for the work and placed in a metal box, which acts as a constant temperature enclosure. Heat is supplied via a heating tape around the box and air circulated by a small fan in the wall of the box. Temperature is controlled and recorded to ± 1°C by an iron-constanton thermocouple and Ether 12-91 anticipatory controller. The two bands considered are each recorded four or five times at each temperature and an average value of the relative absorbance taken. Four or five temperatures are studied between room temperature and about 100°C.

The C-C stretching bands were used in both determinations.

RESULTS AND DISCUSSION

Enthalpy Difference

Plots of $\ln\left(\frac{A_\ell}{A_m}\right)$ versus $\frac{1}{T}$ are shown in Figs. 2 and 3, for the vapour phase of $CHCl_2COCl$ and $CHCl_2COBr$ respectively. The points obtained are very badly scattered and it is only possible to say that for $CHCl_2COCl$ the enthalpy difference between the two stable forms is in the range 100 - 500 cals./mole (Mizushima et al. give a value of 'about 200 cals./mole'). For $CHCl_2COBr$ the difference appears to be less than 100 cals./mole. In both cases the less polar form is the more stable.

No determinations have been made for the liquid state in this work but Mizushima states that for $CHCl_2COCl$ the relative intensity of the two bands remains almost constant from room temperature down to

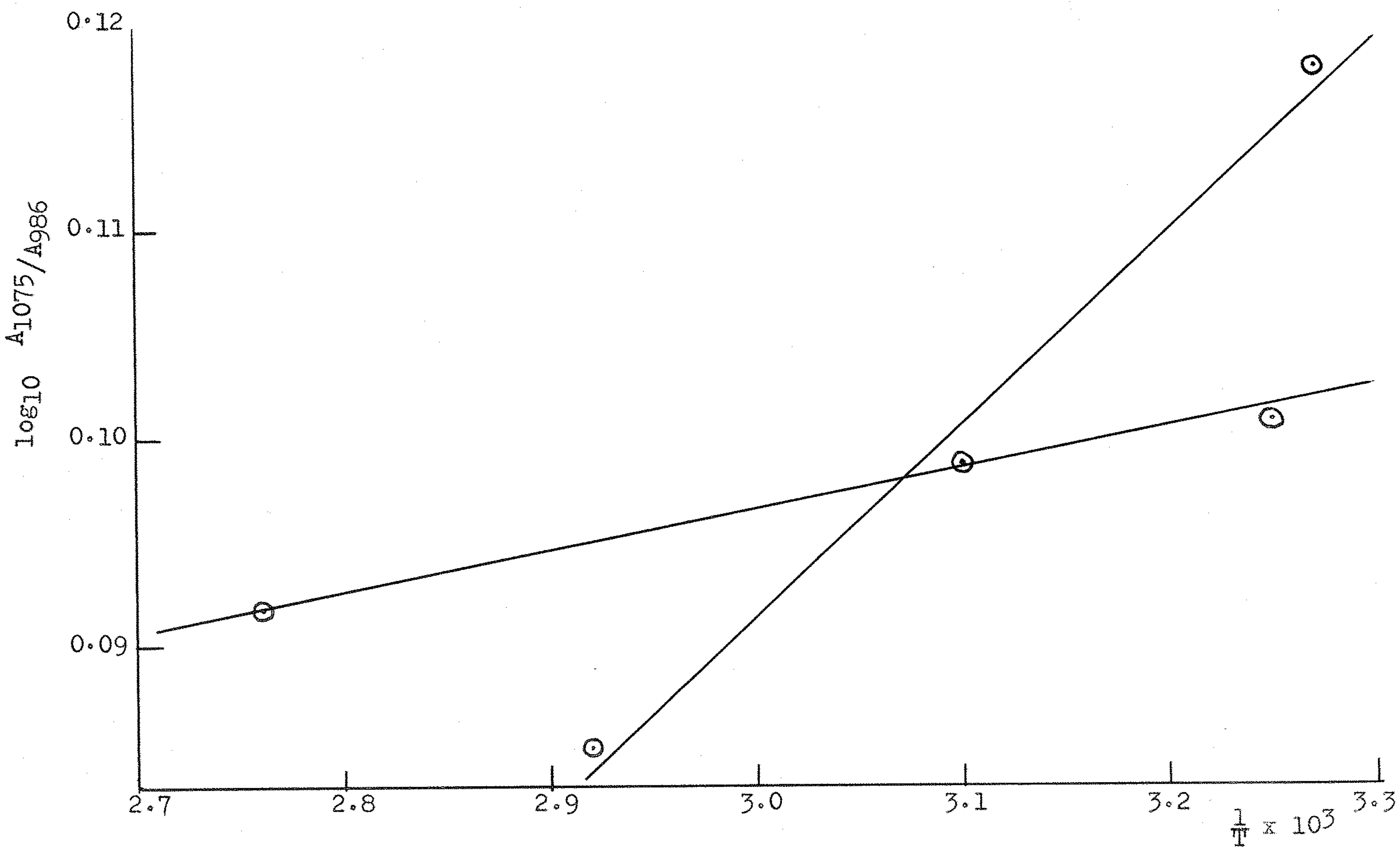


Fig. 2. Enthalpy Difference between rotational isomers of $CHCl_2COCl$ (vapour).

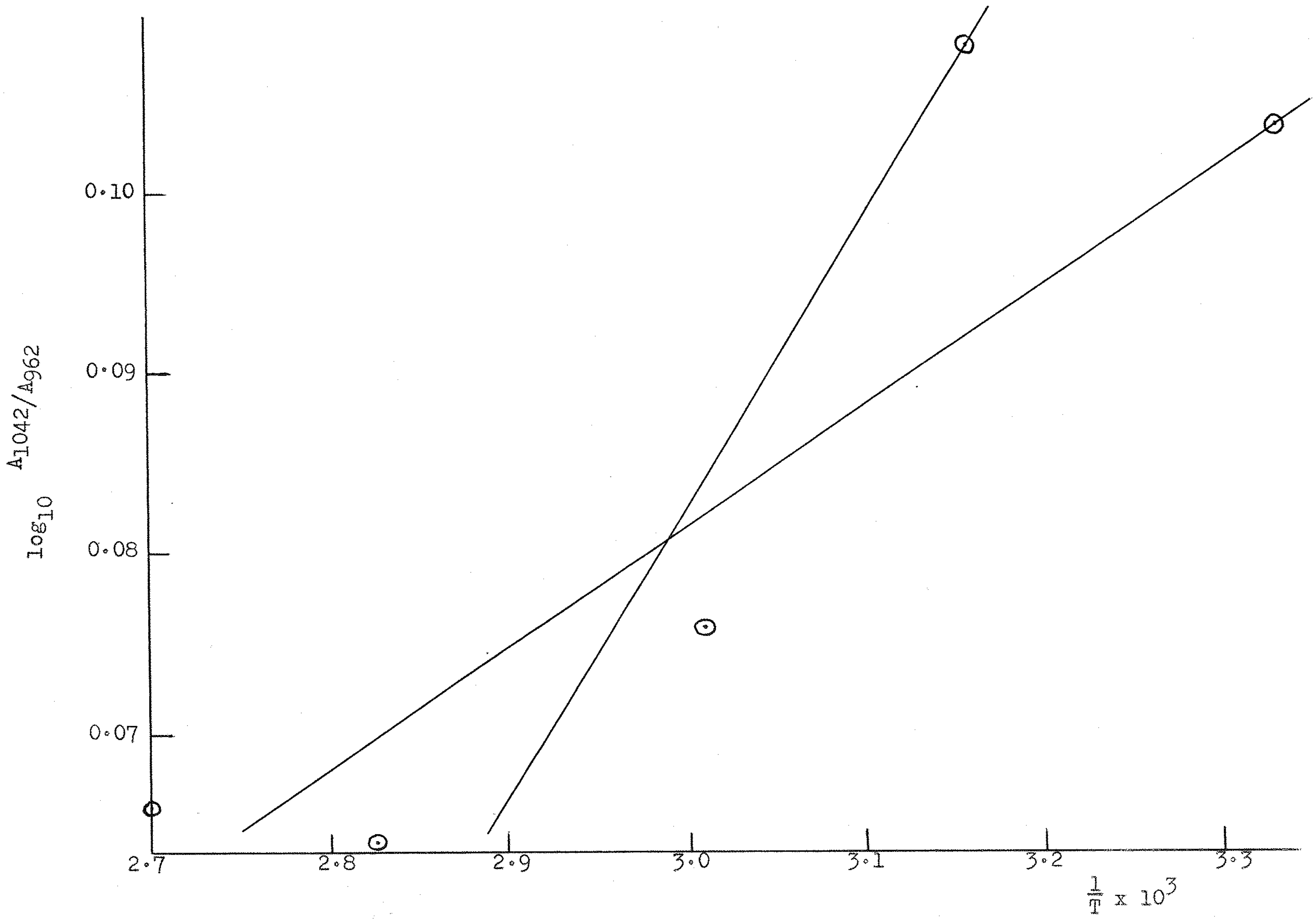


Fig. 3. Enthalpy Difference between rotational isomers of $CHCl_2COBr$ (vapour)

-150°C, indicating that in the liquid the energy difference is negligibly small. (Since we are considering an internal rotation only, Δ H and Δ E will be very similar.)

It seems surprising that, having established this fact, the previous workers were able to reduce the solid spectrum to that caused by the more polar form alone. One would expect to freeze out a mixture of the two forms, as has been found in the present work. The reported solid spectrum is, however, poor and it is doubtful that a true one-isomer spectrum was obtained.

A reduction in intensity of less polar bands has been noticed on passing from the liquid to solid state, suggesting that although very small, the enthalpy difference is finite.

The ease of internal rotation is determined by the height of the energy barrier between the two forms. If this is large and the enthalpy difference is small as shown in Fig.4, then very slow cooling will be required to convert all molecules to the more stable form. This may be seen as follows.

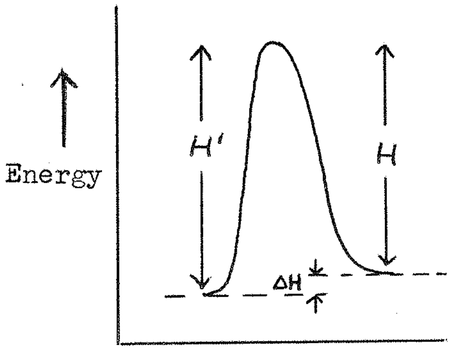


Fig.4. Azimuthal angle.

If a molecule possesses rotational energy in excess of H', equilibration between the two forms is possible. In a certain critical temperature range the energy of the molecule will drop below H', but still be greater than H, so that the conversion, less polar to more polar, is possible, but the reverse process is not. At temperatures below this range no interconversion is possible. Therefore, rapid cooling of the sample through the critical temperature range would prevent complete conversion to the more stable form, and a mixture of isomers would be frozen out, showing a probable reduction in the concentration of the less stable form from that found in the liquid state at room temperature. Also, if the critical range was above the melting point of the compound, this would explain why complete conversion to the more stable form did not occur on melting the sample and recooling it.

Another possible explanation of the effect is that the solid formed was not crystalline. Crowder and Northam report (16) that they were unable to produce a solid sample of 2-Bromo-2-methylpropionyl bromide with molecules in one conformation only. They concluded that since there is an obvious enthalpy difference between the isomers in the liquid state, the solid samples studied were probably not crystalline.

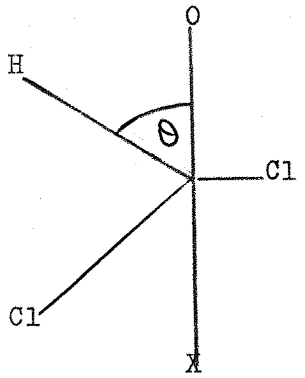
Vibrational Frequencies and their approximate assignments

The observed infrared spectra for the solid and liquid states of the three compounds are shown in Figs. 5, 6 and 7. All spectra are interpreted in terms of the coexistence of two rotational isomers, and assignments are made as to the vibrational mode and molecular conformation responsible for each band.

The assignments to vibrational modes are readily made by comparison with the expected frequencies of the molecular groups, although in certain cases the vibrational analysis indicates considerable mixing of these simple modes.

Conformation assignments are made as previously mentioned, by comparison of solid, liquid, vapour and solution spectra.

The azimuthal angle of internal rotation, θ , referred to in the discussion, is defined as:



X = F, Cl, Br.

and all vibrational frequencies are in cm^{-1}.

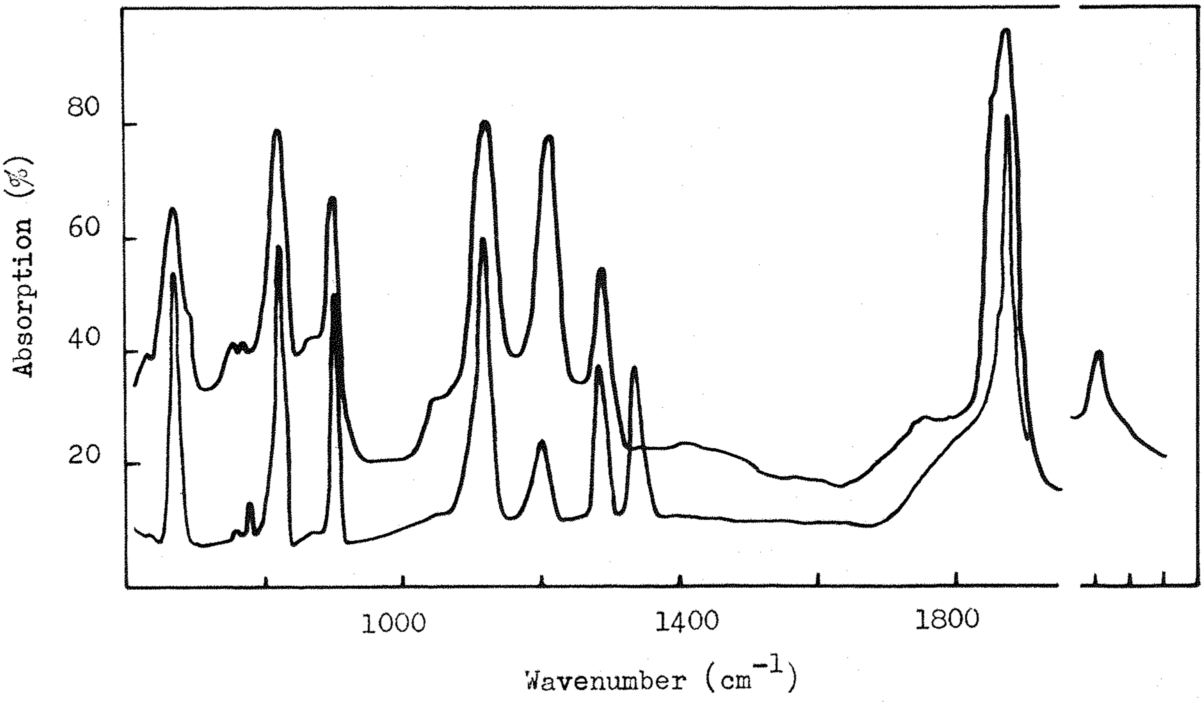


Fig. 5 Infrared spectra of $CHCl_2COF$. a) liquid. b) solid.

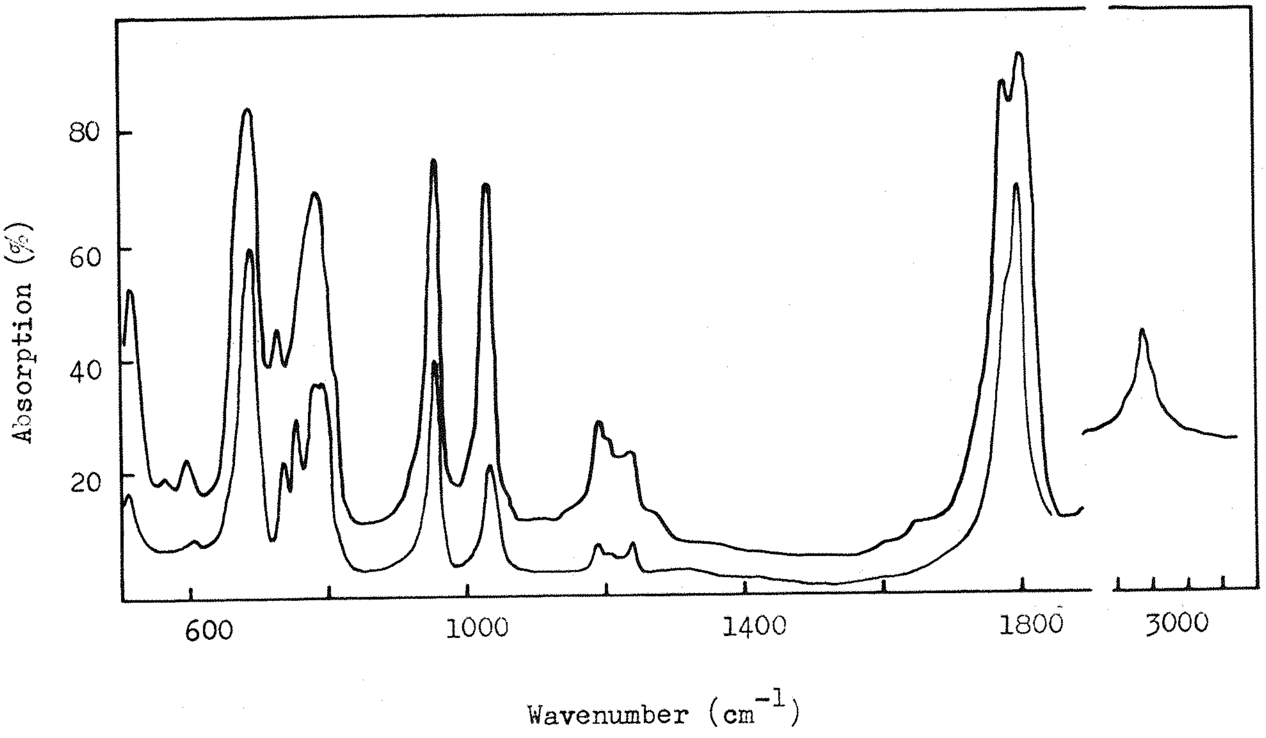


Fig. 6 Infrared spectra of $CHCl_2COBr$. a) liquid. b) solid.

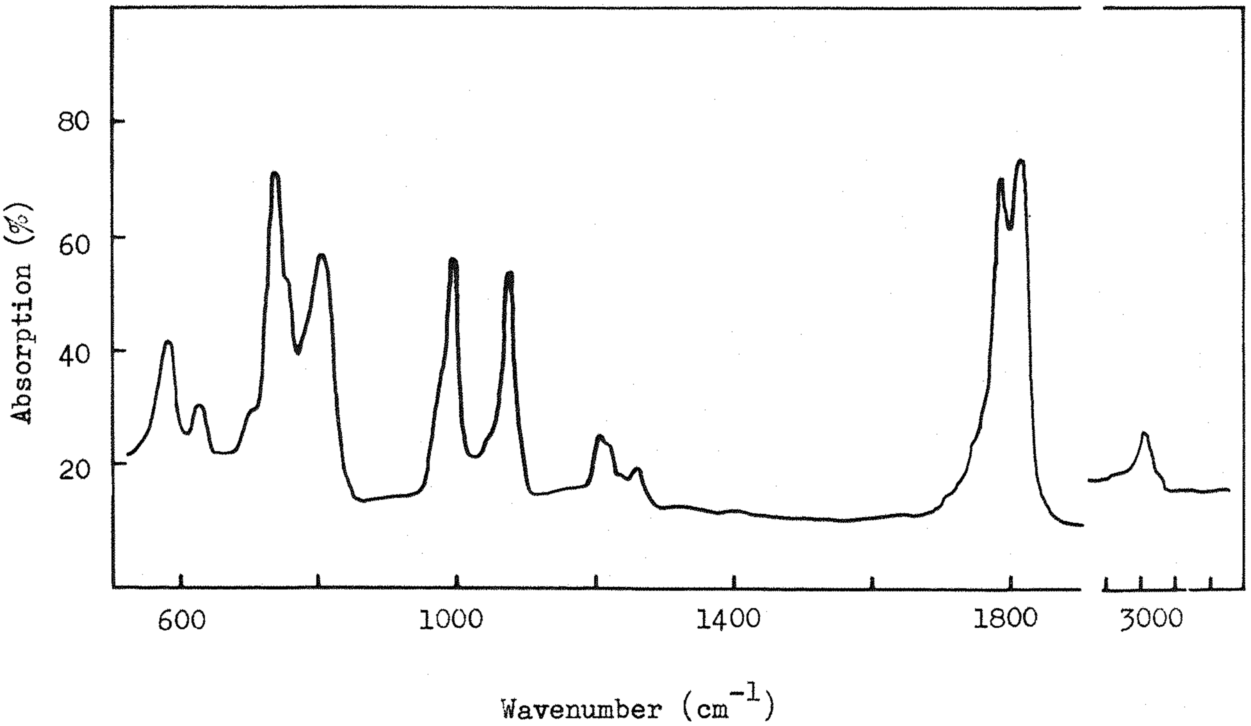


Fig. 7a Infrared spectrum of $CHCl_2COCl$ in the liquid state.

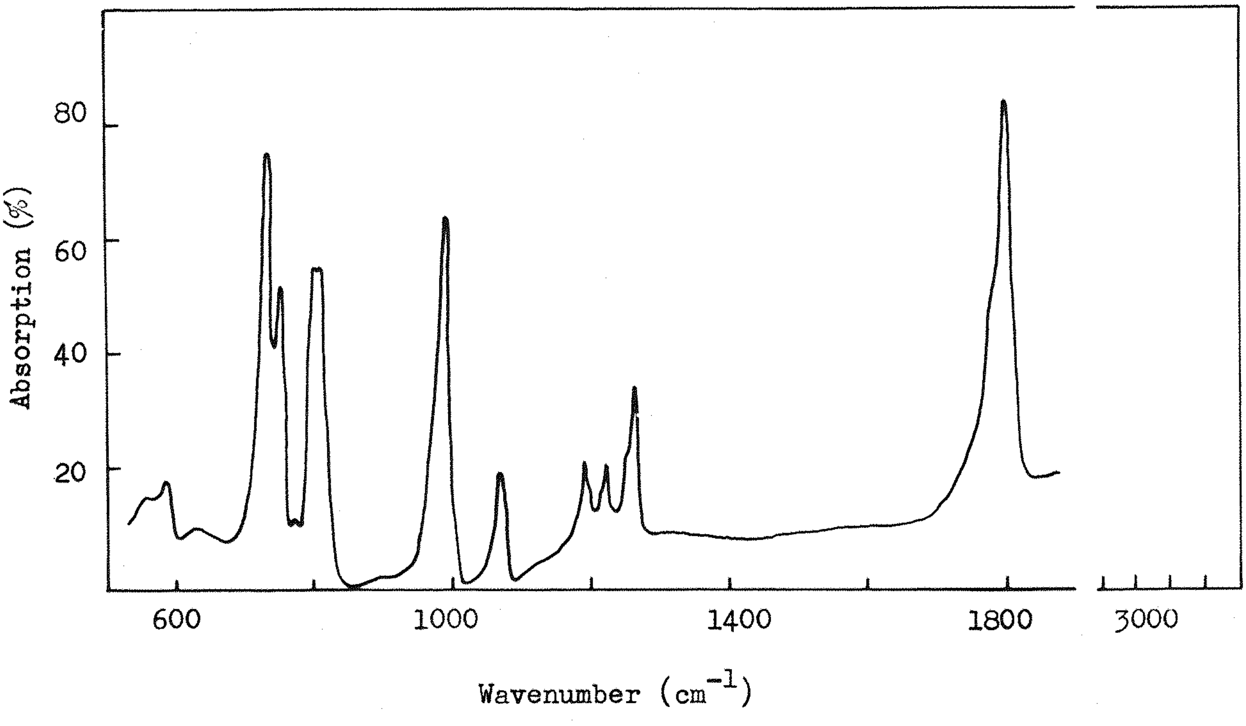


Fig. 7b Infrared spectrum of $CHCl_2COCl$ in the solid state.

Dichloroacetyl fluoride

The observed infrared and Raman frequencies for the compound are given in Table 3 and compared with the calculated frequencies in Table 4. Assignments will be considered in order of decreasing frequency.

An i.r. absorption band at 2985 in the vapour spectrum is assigned to ν (C–H) for the two conformations of the molecule. Due to the small size of the hydrogen atom, it will experience little interaction with the (O–C–F) group on internal rotation and hence this vibration in the two forms will occur with almost the same frequency.

The carbonyl stretching frequency should be somewhat higher than that reported by Mizushima for the acid chloride (1800, more polar) as a result of the very electronegative fluorine atom strengthening the C=O bond. This is in fact found; a strong band occurring at 1859 (liquid) with a strong shoulder evident on its low frequency side. In solvents of high polarity in which the more polar form is stabilised to a greater extent than it is in, for example, carbon tetrachloride the 1859 band increases in intensity at the expense of the shoulder and hence the former is assigned to the more polar form and the shoulder to the less polar. Reference to the solid spectrum indicates that in this state the shoulder is very weak, suggesting that the more polar is the more stable form in the solid. In fact, this spectrum is the 'best' solid spectrum obtained in the series, for conversion to the more stable conformer is almost complete. This is probably due to the enthalpy difference being greater for $CHCl_2COF$ than for the other two molecules.

The region 900-1400 is more complicated. From group frequency considerations, one expects, for each conformation of the molecule, two δ(C-H) bands between 1250 and 1350 cm^{-1}, one ν(C-F) at around 1100-1200 cm^{-1}, and one ν(C-C) band between $\sim$900 and 1000 cm^{-1}. However, coupling of these simple modes may also be expected. A C-F bond stretch will cause a movement of electrons into the C-F bond and hence a resultant change in the C-C (and C-H) bond strength. This coupling is shown in the distribution of potential energy among the diagonal elements of the F matrix, as calculated for each normal mode (Table 5).

The expected eight absorption bands are found in the infrared spectrum of the vapour, at 1370(w). 1342(w), 1282(m), 1250(w), 1214(s), 1111(s), 901(m), 881(m). The Raman spectrum of the liquid gives no clue to their assignments, since only two weak bands occur in the region. Solution and solid spectra do, however, enable a conformational assignment to be made. In passing from CCl_4 to MeCN solution there is a noticeable decrease in intensity of the 1214 cm^{-1} band with respect to the 1111 cm^{-1} band, and these are thus assigned less and more polar respectively. This intensity change is even more marked, going from liquid to solid spectra, and confirms that the more polar is the more stable conformation in the solid. Also with increasing solvent polarity, the 881 cm^{-1} band (which is very weak in the solid) decreases with respect to the 901 cm^{-1} band, and the 1250 cm^{-1} band (not present in the solid) decreases with respect to the 1282 cm^{-1} band. The solid spectrum shows no absorption at 1370 cm^{-1}, but a band of moderate intensity is present at 1332 cm^{-1}. On this evidence the vapour spectrum is assigned:

1370(L), 1342(M); 1282(M), 1250(L); 1214(L), 1111(M);
901(M), 881(L).

Although some coupling of these vibrations seems certain, the strength of the 1214 cm^{-1} and 1111 cm^{-1} absorptions compared to the other six suggests that the normal mode responsible has considerable C-F stretching character, since a change in this bond involves a large dipole moment change and hence intense i.r. absorption.

Three infrared bands occur between 750 and 830 cm^{-1} and it is in this region that the symmetric and asymmetric stretching modes of the (C-Cl_2) group are anticipated (for $CHCl_2COCl$ they occur between 730 and 810 cm^{-1}). Comparison of the optical densities of the 822 cm^{-1} band (liquid) with those of the previously mentioned bands at 898 and 868 cm^{-1}, in the solid and vapour spectra, indicates that the intensity of the 822 band remains almost constant with the change of state. For this reason the band is assigned to both conformations of the molecule. Of the bands at 778 and 763 cm^{-1} the latter decreases in intensity in the solid. The complete assignment is therefore:

TABLE 3.

Spectral Data for $CHCl_2COF$ (cm^{-1})

Vapour I.R.	Liquid I.R.	Liquid Raman	Solid I.R.	Form[a]
2985 m.				M,L
1876 s.	1859 } s.	~1856 (4)	1859 } s.	M
1859 s.	- } s.sh.		- } w.sh.	L
1370 w.				L
1342 w.			1332 m.	M
1282 m.	1280 m.	~1285 (1)	1282 m.	M
1250 w.	1248 v.w.			L
1214 s.	1205 s.	~1213 (1)	1203 m.	L
1111 s.	1112 s.		1120 s.	M
901 m	898 s.		903 s.	M
881 m.	868 w.-m.		870 v.w.	L
826 s.	822 s.	825 (2)	821 s.	M,L
	778 } w.-m.	784 (7)	781 w.	M
762 m.	763 } w.-m.	769 (3)	760 v.w.	L
671 m.-s.	671 m.-s.	678 (7)	673 s.	M
650 } m. 643 }	639 w.-m.	645 (1)	639 w.	L
588 w.				
478 s.	477 m.			m
	456 m.			ℓ
	424 s.	428 (10)		ℓ
	401 s.	404 (10)		m
	293 s.	288 (4)		m,ℓ
	275 s.	275 (3)		m
	243 m.-s.	244 (3)		ℓ
	220 m.	221 (1)		ℓ
	195 s.	193 (3)		m

a. M denotes the more polar form and L the less polar form.
m and ℓ denote very tentative assignments.
w = weak; m = moderate; s = strong; sh = shoulder, in the usual manner.

TABLE 4.

Comparison of observed and calculated frequencies of $CHCl_2COF$ (cm^{-1})

observed frequencies		calculated frequencies				
more polar	less polar	$\theta = 0^o$	$\theta = 45^o$	$\theta = 90^o$	$\theta = 135^o$	$\theta = 180^o$
2985	2985	2938	2937	2936	2937	2937
1876	1859	1784	1786	1788	1785	1783
1342	1370	1255	1260	1267	1266	1258
1282	1250	1210	1202	1191	1205	1215
1111	1214	1165	1171	1177	1153	1141
901	881	917	924	935	943	946
826	826	775	816	841	825	782
778	762	758	722	703	714	760
671	645	664	655	637	644	650
401	424	418	416	405	405	409
293	293	383	367	369	376	383
275	243	277	274	267	267	274
195	220	227	213	192	226	240

TABLE 5.

The distribution of potential energy among the diagonal elements of the F matrix as calculated for each normal mode of $CHCl_2COF$ ($\theta = 0^{\circ}$)

Calculated frequency	Vector of internal coordinates														
	Δr(C–C)	Δr(C–H)	Δr(C–Cl)	Δr(C–Cl)'	Δr(C–F)	Δr(C=O)	$r_{CH}\Delta\alpha$(H–C–Cl)	$r_{CH}\Delta\alpha$(H–C–Cl')	$r_{C-Cl}\Delta\alpha$(Cl–C–Cl)	$r_{C-F}\Delta\alpha$(F–C–O)	$r_{C-C}\Delta\alpha$(C–C–F)	$r_{C-C}\Delta\alpha$(C–C–O)	$r_{C-H}\Delta\alpha$(C–C–H)	$r_{C-Cl}\Delta\alpha$(C–C–Cl)	$r_{C-Cl}\Delta\alpha$(C–C–Cl')
2938		1·0													
1784						1·0									
1255							0·6	0·5							
1210	0·2				0·4					0·1		0·1	0·2		
1165	0·4				0·1		0·1	0·3					0·4		
917	0·3				0·4										
776			0·6						0·1		0·1		0·1	0·1	
758			0·3	0·9											0·2
664										0·5	0·2				
418			0·2	0·2						0·1	0·2				
383				0·1										0·4	0·4
277									0·7						
227											0·2			0·3	0·3

822 (M,L), 778(M), 763(L). The relative intensity of the 784 and 769 cm^{-1} Raman lines supports this assignment.

The change in polarisability of the C-Cl bonds during a symmetric ν(C-Cl$_2$) vibration will be greater than for the asymmetric mode, and greater Raman scattering will therefore occur for this mode. In view of this (and the potential energy distribution (Table 5), the 825 cm^{-1} band is attributed to the symmetric vibration.

C-F bending vibrations are assigned 671(M), 639(L), 477(M), 456(L). The high frequency pair appear to be caused by a vibration in the (F-C-O) plane, since the normal coordinate analysis only considered motions of the fluorine atom in this plane and the agreement between observed and calculated frequencies is quite good. Similarly since no calculated frequencies occur between 450 and 480 cm^{-1}, the lower pair are attributed to vibrations of the group out of the (F-C-O) plane.

The potential energy distribution gives some indication of the skeletal deformations responsible for the low frequency bands. However, for all three compounds studied, the low frequency conformation assignments are made very tentatively. Attempts have been made to record infrared spectra of the solids in the region 200-450 cm^{-1} but the results have been poor. Assignments are suggested from considerations of the infrared and Raman spectra of the liquid, the calculated frequencies, and use of the sum rule (Appendix II). It is hoped that further work (see below) will enable a more precise assignment to be made for all three compounds.

The sum rule may be written as:

$$\sum \nu_{MP^2} = \sum \nu_{LP^2}$$

where the ν_{MP} and ν_{LP} refer to the vibrational frequencies of the more and less polar forms, respectively.

Calculated values of $\sum \nu_{MP2}$ and $\sum \nu_{LP2}$ for $CHCl_2COF$, assuming the assignment in Table 3 to be correct, are $20{\cdot}26 \times 10^6$ and $20{\cdot}30 \times 10^6$ respectively. The agreement is acceptable and adds support to the proposed assignment.

Dichloroacetyl chloride

The observed i.r. and Raman frequencies for this molecule are given in Table 6. A conformational assignment has been made, as in the case of $CHCl_2COF$, by a comparison of solid, liquid, vapour and solution spectra. For frequencies greater than 500 cm^{-1} the assignment is definite and in complete agreement with the previous detailed study by Mizushima et al.(1) Lower frequency data are again very uncertain, being based on rather poor infrared spectra of the solid in the region 200-450 cm^{-1}.

The calculated potential energy distribution (Table 8) indicates the vibrational modes responsible for the observed frequencies. Bands at 3003, 1786, and 1075 cm^{-1} (for the less polar form) may be assigned immediately to ν(C-H), ν(C=O), and ν(C-C) respectively. 1242 and 1224 cm^{-1} bands are attributed to C-H bending

TABLE 6

Spectral Data for $CHCl_2COCl$ (cm^{-1})

Vapour I.R.	Liquid I.R.	Liquid Raman	Solid I.R.	Form
3003	3003		3003	M, L
1961 w.	1961 w.		1980 w.	
1818 v.s.	1808 v.s.	1813	1795 v.s.	M
1786 v.s.	1779 v.s.	1788	1773 m.sh.	L
1252 m.	1253 m.		1266 m.	M
1242 m.	1230 m.	1242	1223 w-m.	L
1224 m.	1214 m.	1214		L
1212 m.	1202 m.		1992 w-m.	M
1075 v.s.	1068 s.		1070 w-m.	L
986 s.	987 s.		995 s.	M
838 m.	804 s.	816	806 s.	M
800 v.s.	785 s.	790	781 w.	L
760 m.	752 s.	762	753 v.s.	M
739 v.s.	734 v.s.		735	L
640 m.	631 m.		629 w.	L
585 s.	575 m-s.	586	583 m.	M
	503 m.	511	505 w.	ℓ
	491 m.	500	489 m.	m
	463 m.	470	466 m.	ℓ
	450 m.		449 m.	m
	414? v.w.	419		ℓ
	338 m.	346	337 m.	m
	284? w.	294	287 w.	m
	262 m.	272	264 w.	ℓ
	253? m.		251 w.	ℓ
	240 m.	250	242 w.	m
		202		ℓ
	177 m.	186		m

TABLE 7

Observed and calculated frequencies of $CHCl_2COCl$ (cm^{-1})

Observed More polar	Observed Less polar	Calculated frequencies				
		$\theta = 0^\circ$	$\theta = 45^\circ$	$\theta = 90^\circ$	$\theta = 135^\circ$	$\theta = 180^\circ$
3003	3003	2937	2937	2936	2937	2937
1818	1786	1747	1748	1750	1747	1745
1252	1242	1254	1256	1260	1259	1255
1212	1224	1172	1173	1175	1179	1181
986	1075	1086	1086	1080	1064	1054
838	800	801	820	833	813	766
760	739	760	743	730	734	762
585	640	597	619	652	695	727
491	503	528	524	515	502	491
	414	397	392	377	372	383
338		383	338	309	330	344
284	262	268	271	259	237	239
177	202	161	155	154	201	214

TABLE 8

The distribution of potential energy among the diagonal elements of the F matrix as calculated for each normal mode of $CHCl_2COCl$ (azimuthal angle θ = 0°)

Calculated frequency	Vector of internal coordinates														
	ν(C–C)	ν(C–H)	ν(C–Cl)	ν(C–Cl')	ν(CO–Cl)	ν(C=O)	$r_{C-H}\Delta\alpha$(H–C–Cl)	$r_{C-H}\Delta\alpha$(H–C–Cl')	$r_{C-Cl}\Delta\alpha$(Cl–C–Cl)	$r_{C-Cl}\Delta\alpha$(O–C–Cl)	$r_{C-C}\Delta\alpha$(C–CO–Cl)	$r_{C-C}\Delta\alpha$(C–C–O)	$r_{C-H}\Delta\alpha$(C–C–H)	$r_{C-Cl}\Delta\alpha$(C–C–Cl)	$r_{C-Cl}\Delta\alpha$(C–C–Cl')
2937		1·0													
1747						1·0									
1254							0·6	0·5							
1172							0·2	0·3					0·7		
1086	0·8				0·2					0·2		0·2			
801	0·1		0·4	0·1					0·2			0·2			
760			0·5	0·8										0·2	0·2
596					0·5					0·2					
528					0·2					0·3	0·1				
397			0·2	0·2								0·2			
383			0·1											0·4	0·4
268									0·7						
161											0·3	0·1		0·2	0·2

vibrations; 800 and 739 cm^{-1} bands to asymmetric and symmetric stretching in the ($C-Cl_2$) group, and the 640 cm^{-1} band to the CO-Cl stretch. There is, as expected, a notable absence of the strong coupling of vibrations exhibited by the H-C-C-F system of $CHCl_2COF$.

Lower frequencies are caused by the various skeletal deformations of the molecule.

Application of the sum rule to the tentative assignment given in Table 6 shows that this assignment is reasonable, the calculated values of $\sum \nu_{MP}2$ and $\sum \nu_{LP}2$ being $18{\cdot}82 \times 10^6$ and $18{\cdot}68 \times 10^6$ respectively.

Dichloroacetyl Bromide

The relevant data for dichloroacetyl bromide is given in Tables 9-11. Figs. 6 and 7 show the great similarity between the vibrational spectra of $CHCl_2COBr$ and those of $CHCl_2COCl$. This is not surprising since chlorine and bromine have similar electronegativities. In view of this, assignments down to 450 cm^{-1} are obvious; it is sufficient to say that the CO-Br stretching vibration occurs at 604 (M) and 571(L) cm^{-1}. Conformation assignments follow the same arguments as for the acid fluoride and chloride, and are again tentative in the low frequency region. Calculated values of $\sum \nu_{MP}2$ and $\sum \nu_{LP}2$ are $18{\cdot}37 \times 10^6$ and $18{\cdot}30 \times 10^6$ respectively and the agreement between observed and calculated frequencies is fairly good.

TABLE 9

Spectral Data for $CHCl_2COBr$ (cm^{-1})

Vapour I.R.	Liquid I.R.	Liquid Raman	Solid I.R.	Form
3000	3000			M,L
1905 w.	1912 w.		1923 w.	
1815 v.s.	1798 v.s.	1807 (2)	1792 v.s.	M
1786 v.s.	1770 v.s.	1784 (2)	– sh.	L
1261 w.				
1242 w.	1244 w.		1245 w.	M
	1227 v.w.			L
1218 m.	1212 w.	~1208 (1)	1212 w.	L
– sh.	1198 w-m.		1195 w.	M
1042 s.	1036 s.	1040 (1)	1042 m.	L
962 s.	963 s.	966 (1)	968 s.	M
794 v.s.	796 s.	801 (2)	796 s.	M
		774 ?	775 m.	L
		744 (5)	737 m.	M
704 v.s.	699 v.s.	697 ?	699 v.s.	L
604 m.	605 w.		605 w.	L
571 w.	~571 v.w.	569 ?	570 w.	M
518 m.	513 m.	517 (2)	517 m.	M
		457 (5)		L
	390 ?		399 w.	ℓ
	368 m.	371 (5)	375 w.	m
	356 m.	358 (2 sh.)	358 w.	ℓ
			351 w.	m
	317 m.	317 (10)	317 m.	ℓ
			302 w.	m
	238 m.	259 (2)	246 w.	m
	217 m.	217 (4)		ℓ
		156 (1)		m,ℓ
		147 (1)		

TABLE 10

Observed and calculated frequencies of $CHCl_2COBr$ (cm^{-1})

Observed frequencies		Calculated frequencies				
More polar	Less polar	$\theta = 0^o$	$\theta = 45^o$	$\theta = 90^o$	$\theta = 135^o$	$\theta = 180^o$
3000	3000	2937	2937	2936	2937	2937
1815	1786	1745	1747	1748	1746	1744
1261	1242	1254	1257	1261	1260	1256
~1200	1218	1173	1173	1175	1181	1185
962	1042	1106	1107	1101	1083	1073
794	774	804	823	835	815	765
741	704	760	745	736	740	762
571	604	604	621	649	694	736
518	457	467	465	453	431	405
370	390	383	380	370	368	383
302	317	364	314	285	313	339
238	217	264	268	246	225	238
156	147	131	128	135	180	182

TABLE 11

The distribution of potential energy among the internal coordinates of $CHCl_2COBr$ (azimuthal angle $\vartheta = 0^{\circ}$) as calculated for each normal mode

Calculated frequency	ν(C-C)	ν(C-H)	ν(C-Cl)	ν(C-Cl)'	ν(CO-Cl)	ν(C=O)	δ(H-C-Cl)	δ(H-C-Cl)'	δ(Cl-C-Cl)	δ(O-C-Cl)	δ(C-CO-Cl)	δ(C-C-O)	δ(C-C-H)	δ(C-C-Cl)	δ(C-C-Cl)'
2937		1·0													
1745						0·9									
1255							0·6	0·5							
1173							0·2	0·3					0·7		
1106	0·7				0·1					0·2		0·2			
804	0·2		0·4	0·1				0·2			0·2				
760			0·5	0·7										0·2	0·2
604					0·1					0·3			0·1	0·1	
467			0·1	0·1	0·3						0·2				
383				0·1										0·4	0·4
364			0·1		0·4										
264									0·7						
131											0·3	0·1		0·2	0·2

Changes in Group frequencies through the series $CHCl_2COX$ are readily explained in terms of inductive effects.

The C=O stretching frequency shows an increase with an increase in the electronegativity of atom X. A more electronegative atom draws more electron density from the oxygen atom into the C=O bond, thus strengthening the bond and increasing the vibrational frequency. It also draws electrons from the C-C bond decreasing the ν(C-C) frequency and this in turn draws electron density from chlorine into the C-Cl bond increasing the $\nu(C-Cl_2)$ frequencies.

The slight decrease in frequency of ν(C=O) from vapour to liquid and liquid to solid is a result of field effects. The partial or complete orientation of dipoles in the liquid or solid state causes an increased polarisation of the C=O bond and a decrease in the observed frequency.

Most interesting is the decrease in the resolution of the two carbonyl stretching bands with increase in the electronegativity of X. This is also explained in terms of field effects. Bellamy and Williams (10) have studied many α-halogenated ketones in which rotational isomerism occurs, and associated the higher ν(C=O) frequency with the conformation in which oxygen and halogen are close together. The interaction of the carbon-halogen and C=O dipoles causes a decrease in polarisation of the C=O bond and increases the vibrational frequency.

In the three molecules $CHCl_2COBr$, $CHCl_2COCl$ and $CHCl_2COF$, the more polar form gives rise to the highest ν(C=O) frequency, suggesting that in each case the oxygen atom is near to the two chlorine atoms in this conformation. But, the chlorine atoms will also experience the interaction, so that the ν (C-Cl) frequency should be greatest when the oxygen and chlorines are close together. In all three compounds the ν(C-Cl_2) vibrations of the more polar form are of highest frequency, again suggesting that this conformation has oxygen and chlorine in close proximity.

The effect of these α-chlorine-oxygen interactions will decrease as the carbonyl bond becomes stronger, i.e. as X becomes more electronegative. Therefore the difference between the carbonyl stretching frequencies of the two stable isomers will decrease with this change, i.e. the resolution of the ν (C=O) bands for the two isomers will decrease going from $CHCl_2COBr \longrightarrow CHCl_2COCl \longrightarrow CHCl_2COF$ (as observed).

The nature of the stable conformations

The forces hindering internal rotation are both steric and electrostatic. Consideration of a model of dichloroacetyl chloride suggests that if the potential energy curve for the internal rotation was the result of purely steric forces, it would have the approximate form shown in Fig. 8 (no significance should be read into the energy barrier heights and energy differences in these figures).

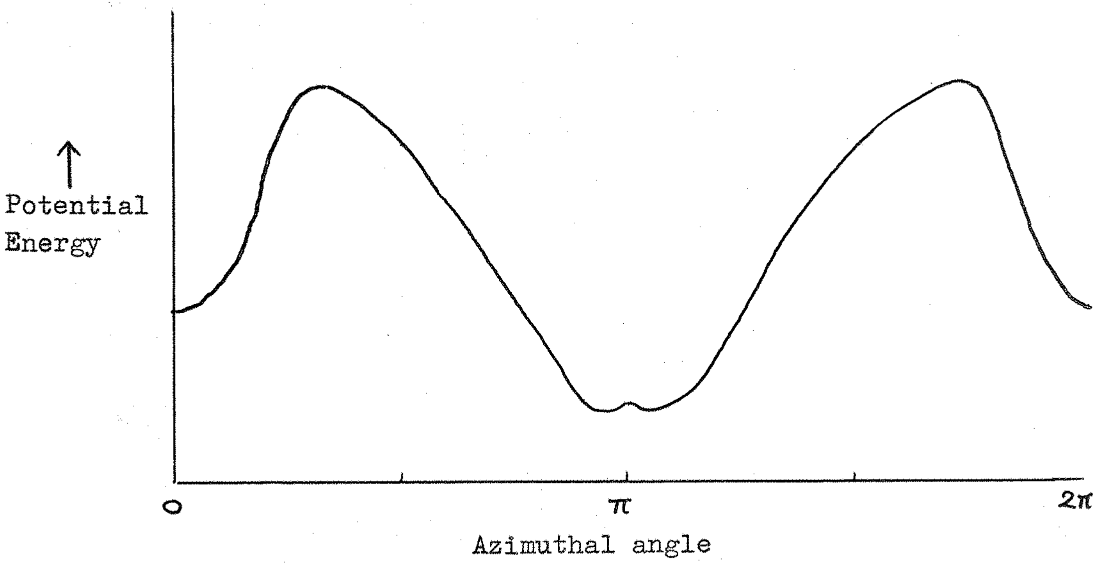


Fig. 8.

To discuss the form of a potential energy curve due to purely electrostatic forces is more difficult, but since oxygen-chlorine interactions will be greater than chlorine-chlorine interactions, a curve of the form indicated in Fig. 9 might be reasonable.

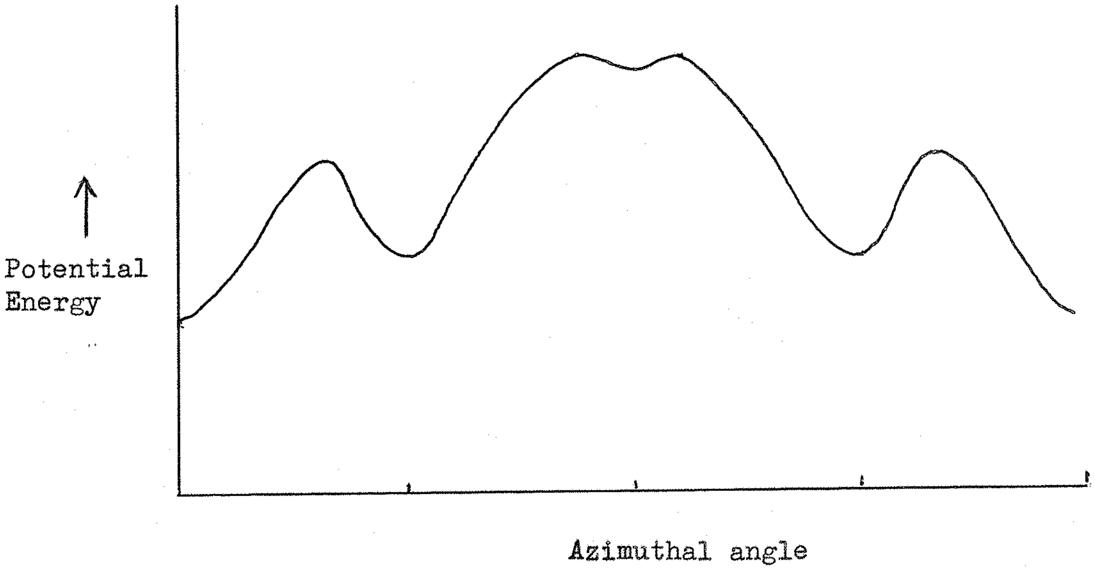


Fig. 9

The total potential energy will be the resultant of the two effects, but it is impossible to give an exact form. It would appear that there is almost certainly a stable conformation with an azimuthal angle $\theta \sim 0^{\circ}$, and there is the possibility of other stable forms with azimuthal angles θ of approximately 90° and 180°. These are the three possible conformations considered by Mizushima et al.and calculated values for the dipole moment of the molecule suggest the conformation $\theta = 0^{\circ}$ to be the less polar.

A similar situation is expected for dichloroacetyl bromide, for here again in the steric interactions the halogen atom is larger than the oxygen atom and in electrostatic terms the oxygen-chlorine interactions greater than those between bromine and chlorine.

For dichloroacetyl fluoride there will still be the possibility of stable conformations at approximately 0°, 90° and 180°, but the small size and large electronegativity of the fluorine atom might be expected to change the order of stability of the conformers.

Mizushima et al. found a steady increase in the dipole moment of $CHCl_2COCl$ from $\theta = 0^\circ$ to $\theta = 180^\circ$, and since the C-F and C-Br bond moments are very similar to that of the C-Cl bond (C-F, 1·4D.; C-Cl, 1·5D.; C-Br, 1·4D.,(C-H, 0·4D.)(11)) the acid fluoride and acid bromide will show a similar increase in dipole moment.

We may therefore consider the following three possibilities for each molecule:

a) less polar $\theta \sim 0^\circ$; more polar $\theta \sim 90^\circ$
b) less polar $\theta \sim 0^\circ$; more polar $\theta \sim 180^\circ$
c) less polar $\theta \sim 90^\circ$; more polar $\theta \sim 180^\circ$

and it may be noted that in each case the more polar conformation has oxygen and the two chlorines close together, in agreement with the previous explanation of relative carbonyl frequencies.

Unfortunately the agreement between observed and calculated frequencies is not close enough for a comparison to confirm one of these arrangements, but it is hoped to refine the calculated frequencies in the near future (see following section).

The product rule is therefore our only means of ascertaining the probable nature of the stable conformations. It states that

$$\frac{\prod \nu_{MP}^2}{\prod \nu_{LP}^2} \qquad \frac{|G(MP)|}{|G(LP)|}$$

where $\prod$ denotes a continuing product, and G(MP) the G matrix for the more polar form.

The derivation of this equation involves the assumption that there are no significant cis-interactions in the molecule, and evaluation of its left-hand side is dependent on the uncertain conformational assignments. Any conclusions drawn must therefore be tentative. Table 12 gives the relevant data for each molecule (a), b), and c) refer to the three arrangements discussed above).

Considering dichloroacetyl chloride first, the results suggest that arrangement a) is correct. It is thus concluded (once again in agreement with Mizushima) that the less polar conformation of $CHCl_2COCl$ has oxygen in the cis-position with respect to hydrogen ($\theta = 0^\circ$),and that the more polar form is obtained from this by an internal rotation of about 90°.

A somewhat different situation is apparent for dichloroacetyl

Molecule	$\frac{\prod \nu_{MP}^2}{\prod \nu_{LP}^2}$	$\lvert G(MP)\rvert$ / $\lvert G(LP)\rvert$		
		a)	b)	c)
$CHCl_2COF$	1·50	0·57	1·06	1·86
$CHCl_2COCl$	0·45	0·57	1·20	2·10
$CHCl_2COBr$	1·39	0·58	1·32	2·28

Table 12. Product rule data for the series $CHCl_2COX$

bromide for although the less polar conformer is still that with $\theta = 0^\circ$, the more polar form is obtained by an internal rotation of about 180°. The change from acid chloride to acid bromide therefore causes a reversal in the stabilities of conformations, $\theta = 90^\circ$ and $\theta = 180^\circ$, which in terms of steric interactions is quite understandable.

The product ratio for $CHCl_2COF$ does not agree too well with the calculated determinant ratios, but it suggests a form having $\theta = 180^\circ$ coexisting with a less polar conformation for which θ is either about 0° or approximately 90°.

Future work

This study of the dichloroacetyl halides is obviously incomplete in its present form. The initial object of the project was to use the product rule and the calculated vibrational frequencies to indicate the nature of the stable conformations existing in the compounds. Without a positive conformational assignment, of all observed frequencies, this is impossible. It is hoped to remedy this situation in the near future by measuring the Raman spectra of solutions of the compounds. This should be relatively simple using the argon ion laser recently coupled with the Carey spectrometer.

Having achieved this, another obvious step will be to improve the agreement between calculated and observed frequencies (remembering the limitations discussed under 'Vibrational Analysis'). Since the work done to date suggests that the less polar conformation of $CHCl_2COCl$ is almost certainly that with azimuthal angle $\theta = 0^\circ$ it is intended to use Schachtschneider's program FPERT to perturb the Urey-Bradley force field and achieve agreement between observed and calculated frequencies for this case. The new force constants thus generated will then be used to calculate more accurate frequencies for the other conformations of this molecule and for all conformations considered for the acid fluoride and bromide.

ACKNOWLEDGEMENTS

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Appendix I.

Computation of the vibrational frequencies

Three programs have been used in the construction and solution of the vibrational secular equations. They have been shown to be correct, and if any error is present in the reported data, it is a result of human error in preparing data for the computer.

a) GMAT (J.H. Schachtschneider)

The program uses the Wilson s-vector method (12) to construct the transformation B from Cartesian coordinates to a set of internal coordinates R.

$$R = Bx$$

G, the inverse kinetic energy matrix in internal coordinates is then computed by

$$G = BM^{-1}B'$$

where M is a diagonal matrix of the reciprocal masses of the atoms (ref. (13) gives a proof of this equation).

The kinetic energy T is given by

$$2T = \mathring{R}'G^{-1}\mathring{R}$$

b) UBZM (J.H. Schachtschneider)

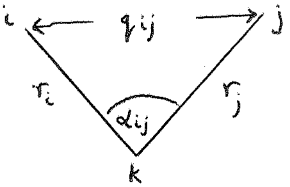
This program constructs the Urey-Bradley F matrix such that the potential energy V in internal coordinates is given by

$$2V = R'FR.$$

The problem is simplified by arranging the Urey-Bradley force constants as a vector $\overset{\top}{\underset{\perp}{\phi}}$ and defining a transformation Z as

$$F = Z \overset{\top}{\underset{\perp}{\phi}}$$

The matrix Z may be assembled by summation of the contributions of various sub-configurations of a molecule to the Z matrix. For example, if one considers a GEM sub-configuration where atoms i and j are bonded to a common atom k, then the internal coordinate Δq_{ij} may be expressed as:

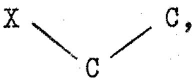
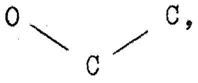
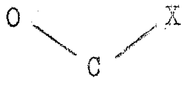
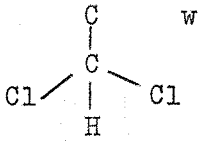


$$\begin{aligned}\Delta q_{ij} = {} & S_{ij}(\Delta r_i) + S_{ji}(\Delta r_j) \\ & + (t_{ij}t_{ji})^{\frac{1}{2}}(r_j/r_i)^{\frac{1}{2}}(r_i \Delta\alpha_{ij}) \\ & + \frac{1}{2\,q_{ij}}\Big\{ t_{ij}^{2}(\Delta r_i)^2 + t_{ji}^{2}(\Delta r_j)^2 - S_{ij}S_{ji}(r_j/r_i)(r_i \Delta\alpha_{ij})^2 \\ & - 2t_{ij}t_{ji}(\Delta r_i \Delta r_j) + 2t_{ij}S_{ji}(r_j/r_i)(\Delta r_i r_i \Delta\alpha_{ij}) \\ & + 2t_{ji}S_{ij}(\Delta r_i\, r_i \Delta\alpha_{ij})\Big\}\end{aligned}$$

where $S_{ij} = (r_i - r_j \cos\alpha_{ij})/q_{ij}$

and $t_{ij} = (r_j \sin\alpha_{ij})/q_{ij}$

Such a relationship introduces the force constants F_{ij}^{l} into the quadratic terms, and the coefficients in the relationship are the contributions of Δq_{ij}(GEM) to the Z matrix (ref.(14) gives fuller details).

For the molecules $CHCl_2COX$ the contributions from three GEM configurations    and one TETRA configuration  were considered.

c) GVIB (J.H. Schachtschneider)

Having expressed the vibrational potential and kinetic energies in terms of internal coordinates we need the transformation from internal coordinates to normal coordinates Q

$$R = LQ \text{ such that}$$
$$2T = \mathring{Q}'E\mathring{Q}$$
$$2V = Q'\Lambda Q$$

where E is a unit matrix and Λ is a diagonal matrix.

In this coordinate system the vibrations are simple harmonic and mathematically independent.

The frequencies ν_i of these so-called normal vibrations are given by the diagonal elements λ_i of

$$\lambda_i = 4\pi^2 \nu_i^2$$

The secular equation is

$$GFL = L\Lambda$$

and the secular determinant

$$\left| GF - \lambda E \right| = 0$$

The GVIB program solves the secular equation by the method of successive orthogonalisation outlined by Wilson (12) followed by a Jacobi diagonalisation. Schachtschneider has also programmed other methods of solution of the secular equation.

Appendix II

The sum and product rules (15)

It will be seen from the above that if the solutions of this secular equation are λ_1, λ_2 - - - - , λ_n, then

$$\sum_{i=1}^{n} \lambda_i = \sum_{k,\ell=1}^{n} G_{k\ell} F_{k\ell}$$

Since in this analysis we are neglecting cis interactions, all the elements $F_{k\ell}$ corresponding to $G_{k\ell}$ containing the azimuthal angle θ vanish and the right-hand side is therefore independent of the degree of internal rotation, i.e.

$$\sum_{i=1}^{n} \lambda_i = \text{constant}$$

Therefore, using $\lambda_i = 4\pi^2 \nu_i^2$ we have

$$\sum_{i=1}^{n} \nu_i^2 = \text{constant}$$

This is the sum rule for rotational isomers.

The product of normal frequencies of a molecular configuration can be expressed:

$$2\pi \prod_{i+1}^{n} \nu_i = \left(|G| \, |F| \right)^{\frac{1}{2}}.$$

Neglecting cis interactions the F matrix becomes common to both of the rotational isomers and we have for the frequencies ν_i and ν_i' of the two isomers the relation:

$$\prod_{i=1}^{n} \nu_i \Big/ \prod_{i=1}^{n} \nu_i^1 = \left(\left| G \right| / \left| G' \right| \right)^{\frac{1}{2}}.$$

Appendix III

Evaluation of the G determinant

It can be shown (12) that the determinant of the G matrix is zero, if there exists a redundancy relationship among the coordinates in which G is expressed. In considering the dichloroacetyl halides we have used as internal coordinates the six bond angles in the tetrahedral unit $C-CHCl_2$ and the three coplanar bond angles in the C-COX unit. There is a redundancy relationship between the angles in both of these sets. Therefore, in order to use the product rule, it is first necessary to transform the G matrix to a set of coordinates in which the redundancies are removed. A simple diagonalisation is such a transformation as will be seen.

Since G is a symmetric matrix,it may be diagonalised by an orthogonal matrix D

$$GD = D\Gamma$$

where Γ is the diagonal matrix. This may be rewritten as

$$(G - \Gamma E)D = 0 \qquad (2)$$

The diagonalisation is equivalent to a transformation from the internal coordinates R to new coordinates

$$\Sigma = D'R$$

Assuming a redundancy relationship T exists among the internal coordinates R, i.e.

$$TR = 0,$$

it can be shown (12) that exactly the same linear combination of elements in any row or column of the G matrix also vanishes

$$TG_K = 0$$

where G_K is a row or column in the G matrix. But a redundancy must produce a zero eigenvalue Γ_K in the diagonal matrix Γ. Equation (2) can therefore only be true if the corresponding eigenvector D_K is equivalent to the redundancy condition, i.e.

$$D_K' = cT$$

where c is a constant.

The new coordinate Σ_K is therefore equal to zero, since

$$\Sigma_K = D_K'R = cTR = 0.$$

In this way diagonalisation removes the redundancy, and the determinant of the G matrix may be found by neglecting the zero eigenvalue in and computing the product of the non-zero eigenvalues.

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