SPECTROSCOPIC STUDIES OF SOME UNSATURATED CARBONYL

COMPOUNDS

(with particular reference to conformations of $\propto \beta$ unsaturated carbonyl compounds)

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A thesis submitted in part fulfilment of the requirements for a C.N.A.A. Ph.D. degree



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INDEX

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	Page
Acknowledgements	(ii)
Summary	(iii)
Chapter I Introduction A General Introduction B Methods for the Study of Conformations C The Conformations of Genusaturated Carbonyl	1 2 4
Compounds and Related Compounds D The Calculation of Thermodynamic Functions	13 18
Chapter II Experimental A Purification of Compounds B Vibrational Spectroscopy C N.M.R. Spectroscopy D Mass Spectrometry	25 26 30 32 32
Chapter III Vibrational Spectroscopy A Rotational Fine Structure and Contours of Infrared Bands in the Vapour State B Variable Temperature Infrared Measurements C Assignment of Bands	33 34 53 75
Chapter IV Nuclear Magnetic Resonance Spectroscopy A Determination of Parameters in Three Spin Systems and Other Systems B Temperature and Solvent Studies	112 114 130
Chapter V Mass Spectrometry A $\propto \beta$ -unsaturated aldehydes and ketones B $\propto \beta$ -unsaturated esters	147 148 153
Chapter VI Discussion of Results	9ز1
Appendices Appendix I Computer Programs Appendix II Statistical Analysis of	
Results Appendix III Courses attended	193 196

1

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SUMM ARY

 α_{β} -unsaturated carbonyl compounds may exist in <u>s-trans</u> and <u>s-cis</u> or possibly non-planar forms.



Acraldehyde ($CH_2=CH-CHO$) and <u>trans</u>-crotonaldehyde ($CH_3CH=CH-CHO$) appear to exist in the <u>s-trans</u> conformation on the basis of measurements of resolved rotational fine structure of certain infrared bands in the vapour state and measurements of infrared band intensities at a series of temperatures in the vapour and solution state:

Methyl vinyl ketone $(CH_2=CH-CO-CH_3)$ and ethylideneacetone $(CH_3CH=CH-CO-CH_3)$ appear to exist in equilibrium mixtures of <u>s-cis</u> and <u>s-trans</u> conformers based on infrared intensity measurements in the vapour and solution states at different temperatures.

Methyl acrylate $(CH_2=CH-COOCH_3)$, ethyl acrylate $(CH_2=CH-COOC_2H_5)$, methyl <u>trans</u>-crotonate $(CH_3CH=CH-COOCH_3)$ and ethyl <u>trans</u>-crotonate $(CH_3CH=CH-COOC_2H_5)$ also appear to exist in <u>s-cis</u> and <u>s-trans</u> conformers, based on infrared intensity measurements in solution and vapour states (useful for acrylates only) at different temperatures.

In the ketones and esters studied the <u>s-trans</u> conformer is considered to be more stable. The best values of the additional enthalpy of the <u>s-cis</u> conformers of the ketones and methyl esters

(111)

are given below:-

Compound	ΔH^{O} (enthalpy d	lifference)
	solution in carbon	vapour
	(-110° to 40°)	(20° to 200°)
Methyl vinyl	461 <u>+</u> 23 cal. mol ⁻¹	565 <u>+</u> 52 cal. mol ⁻¹
ketone	$\left(\frac{1.93 \pm 0.10 \text{ KJ mol}^{-1}}{1}\right)$	$(2.36 \pm 0.21 \text{ KJ mol}^{-1})$
Ethylidene-	513 ± 52 cal. mol ⁻¹	$585 \pm 46 \text{ cal. mol}^{-1}$
acetone	$(2.14 \pm 0.21 \text{ KJ mol}^{-1})$	$\left(\frac{2.45 \pm 0.19 \text{ KJ mol}^{-1}}{2.45 \pm 0.19 \text{ KJ mol}^{-1}}\right)$
Methyl .	315 <u>+</u> 45 cal. mol ⁻¹	400 cal. mol^{-1}
acrylate	$\left(\frac{1.32 \pm 0.19 \text{ KJ mol}^{-1}}{1.32 \pm 0.19 \text{ KJ mol}^{-1}}\right)$	(1.67 KJ mol ⁻¹)
Methyl trans-	521 ± 24 cal. mol ⁻¹	•
crotonate	$\left(2.18 \pm 0.10 \text{ KJ mol}^{-1}\right)$	ж. Ф

Assignments of the vibrational modes of all these compounds are discussed. The esters do not reveal two carbonyl bands corresponding to the two conformers whereas two carbonyl bands are observed for the ketones when two conformers are present. This can be rationalised empirically by comparison with 2-furan derivatives of esters and ketones.

The N.M.R. parameters of vinyl and ethylidene groupings require 'second order' treatments of differing complexity depending on the ratios of the appropriate chemical shift differences to coupling constants. An averaged spectrum for the two conformers is observed even at temperatures of -100° because of the relatively long time scale of the N.M.R. experiment. This limits the information which can be obtained on conformational equilibrium of these compounds by N.M.R.

The mass spectral fragmentation patterns are considered as a basis for the characterisation of $\mathcal{A}\beta$ -unsaturated carbonyl compounds.

(17)

These studies provide confirmation that the energy associated with electron impact is too large to reveal any evidence on <u>s-cis</u> <u>s-trans</u> isomerism.

The major factor contributing to the position of equilibrium between <u>s-trans</u> and <u>s-cis</u> conformers in $\alpha\beta$ -unsaturated carbonyl compounds appears to be steric repulsion. CHAPTER I

INTRODUCTION

- A General Introduction B Methods for the Study of Conformations
- C The Conformers of κβ-unsaturated Carbonyl Compounds and Related Compounds
- D The Calculation of Thermodynamic Functions

THE OBJECT of the present work is to interpret spectra of certain *AB*-unsaturated carbonyl compounds and to attempt to relate these spectra to structure and conformational equilibria within these compounds.

The vibrational spectra of these compounds can provide information on molecular structure from the rotational fine structure and contours of infrared bands in the vapour state. Variable temperature infrared measurements can provide information on possible conformational equilibria; the difference in enthalpy between two conformers (ΔH°) may be calculated from these measurements.

The nuclear magnetic resonance spectra are also dependent on conformations and conformational equilibria, and variable temperature N.M.R. measurements may provide further information.

Mass spectral fragmentation patterns are less likely to be dependent on conformational equilibria, but will be considered in relation to the characterisation of this class of compounds.

In order to set the present study in a general context, a review of some of the principle features of the broad field of conformational equilibria will be presented.

A GENERAL INTRODUCTION

In the early part of this century, it was believed that rotation about single bonds was entirely unhindered. However, in 1936, it was shown¹ that calculations of the enthalpy and entropy of ethane based on statistical mechanics were inconsistent with calculations based on calorimetric values. These differences were interpreted on the basis of a barrier to rotation about the C-C single bond of about

- 2 m

3 Kcal mol⁻¹ (12.0 KJ mol⁻¹). As one methyl group in ethane rotates through 360° relative to the other, three equal energy minima and three equal energy maxima occur corresponding to the staggered (I) and eclipsed (II) forms of ethane.



In n-butane, a similar situation exists when considering rotation about the central C-C bond, but in this case, the maxima have different energies to each other, because of differences in the mutual repulsion of two methyl groups compared with the repulsion between a single methyl group and a hydrogen. The minima are also at different energies to one another.



eclipsed (CH3,CH3)



staggered (gauche)



Oxygenated olefins are an important class of compounds in which conformational equilibria can exist. These compounds are produced in the petrochemical industry as monomers for the manufacture of polymers and as intermediates in other commercial processes. In order to characterise their spectra for analytical purposes it is necessary to consider the possibility of conformational equilibria which can lead to a multiplicity of bands.

The realisation that the spatial arrangement of atoms influences chemical reactions and physical properties of molecules has resulted in an increase in the study of conformations. Polymers have very different properties depending upon their structure and conformation. Thus atactic polymers tend to be soft gummy materials, isotactic polymers are highly ordered crystalline materials and syndiotactic polymers have intermediate properties^{2,3}. Information on the conformations of nucleic acids is clearly important in order to understand genetic processes. It is often difficult to determine the conformations of large molecules and the study of smaller molecules is necessary in order to determine the important factors in conformer stability.

B METHODS FOR THE STUDY OF CONFORMATIONS

The following account briefly summarises the main methods used in the study of molecular conformations. A more detailed summary of the

- 4 -

applications of some of these methods will be provided in relation to & - unsaturated carbonyl compounds and related molecules. 1. Calorimetry This method involves the use of a bomb calorimeter. From the rise of temperature when a compound is ignited under a pressure of oxygen, the heat of combustion can be determined. The expected heat of combustion can be determined assuming no internal rotation, and any difference is caused by the higher enthalpy of one of the conformers. This method, however, yields inaccurate results because of the small enthalpy difference (ΔH°) between conformers (100 to 1 000 cal mol⁻¹ (400 to 4 000 J mol⁻¹)) compared with the total heat of combustion (1 000 Kcal mol⁻¹ (4 000 KJ mol⁻¹)). The entropy can also be determined calorimetrically and the experimental value is compared with that obtained from statistical thermodynamics based on spectroscopic measurements. One of the possible explanations of a lower calorimetric value is rotation about a single bond. This method is useful where barriers to rotation are about 3 Kcal mol⁻¹ $(12 \text{ KJ mol}^{-1}).$

2. <u>Dipole Moments</u> When two or more non-identical atoms are bonded together, the centre of negative and positive charge does not normally coincide and an electric dipole results. If two or more conformers are present, they will normally have different dipole moments. By comparing the observed value of the dipole with that calculated, amounts of different conformers can be estimated. Variation in temperature should reveal changes in the dipole of a molecule with different conformers as the position of equilibria

.

3. <u>Molar Kerr Studies</u> When a voltage is applied to a dielectric medium, the refractive index of the medium at a given wavelength becomes different in directions parallel and perpendicular to the field at that wavelength. This difference between the refractive index parallel and perpendicular to the field can be calculated in terms of the electric field, the wavelength and the Molar Kerr constant. The Molar Kerr constant can be calculated for a given conformer as a gas, liquid or in solution. These constants usually differ sufficiently from one conformer to another to indicate the approximate position of an equilibrium.

4. <u>Dielectric Relaxation Studies</u> A polar molecule aligns itself in an electric field. On removal of an applied electric field from a molecule within which free or almost free rotation can occur, the rotating part of the molecule becomes randomly orientated before the molecule as a whole becomes randomly orientated.

5. <u>Ultrasonic Techniques</u> (often called accoustic methods). As sound waves are passed through a liquid, the excess pressure at any point will alternate periodically because in each cycle the liquid is successively compressed and decompressed. This results in a periodic variation in the temperature during the wave. If a molecular process can occur which products a difference in enthalpy (e.g. a chemical equilibrium, a change in vibrational or rotational level, a conformational change etc.), these small temperature variations result in changes in the equilibrium position. At low accoustic frequencies, the equilibrium and the sound waves can remain in phase. At high frequencies, the reaction rates are too slow to respond during the individual waves. Both of these situations result in no net change in energy. However, at an intermediate frequency dependent on the rate of forward and reverse reactions, the

- 6 -

equilibrium lags behind the sound wave. The molecules in equilibrium receive enthalpy during the temperature crest and give out enthalpy during the temperature trough caused by the sound wave. This results in a decrease in the sound wave intensity as the wave travels through the liquid. The frequency, at which the loss of energy is a maximum, may be related to the rate constants of the forward and reverse reactions. By carrying out variable temperature studies, values of the enthalpy and entropy of activation can be determined from which very approximate values of ΔH and ΔS can be derived.

6. Electron Diffraction A beam of electrons from a hot filament is monochromatised using a stable accelerating potential. This beam traverses a magnetic focusing system and then passes through a sample of gas at low pressure (10⁻⁵mm of Hg). The electron beam is diffracted by the sample molecules because the wavelength of the electrons is of the same order of magnitude as the internuclear distances in molecules. A radial diffraction pattern is produced which consists of three parts, incoherent atomic scattering, coherent atomic scattering and coherent molecular scattering, the latter being important in determining molecular structure. From the coherent molecular scattering, interatomic distances can be determined. Thus, if a molecule can exist in two or more conformations, interatomic distances will be different and should be observed in the diffraction pattern. This method is only applicable to relatively small molecules because with larger molecules a continuum representing several similar interatomic distances is observed and different conformers cannot be distinguished.

- 7 -

7. X-Ray Diffraction This method is limited to compounds in the solid state. Exact structures for complicated molecules can often be determined from studies of single crystals. Crystals act as diffraction gratings to X-rays. A diffraction photograph of a single crystal consists of an array of spots whereas a photograph of a powder produces a series of arcs. From the position of these spots or arcs the symmetry of the molecule can usually be derived without too much difficulty. To obtain molecular parameters requires many different diffraction photographs. The method then requires an approximate structure, from which a better solution can be obtained by an iterative procedure. The final data is often presented in the form of a Fourier electron density map. The ability of any medium to scatter X-rays is proportional to the number of orbital electrons. Hence the position of a light atom in a solid is difficult to establish. It is unusual to find more than one conformation present in the solid state, and if this occurs it is difficult to detect by X-ray techniques.

8. <u>Neutron Diffraction</u> The principles of this method are much the same as those of X-ray diffraction. It is often used as a complementary technique to X-ray diffraction to determine the position of hydrogen atoms in the structure since one of the important differences is that neutrons are scattered by nuclei and all elements scatter by a similar amount. The method requires a source of a strong beam of monochromatic neutrons (such as a nuclear pile).

9. <u>Neutron Spectroscopy</u> This method also requires a strong beam of monochromatic neutrons. When neutrons come into contact with molecules in an excited state, the neutrons can acquire extra energy while the

• 8 -

molecule drops from a higher vibrational level to the ground state. Since neutrons travel at a speed related to their energy, by using a time of flight detector, it has been found possible to observe new bands in the neutron time of flight spectrum corresponding to loss of vibrational energy. This method has been found particularly suitable for determining torsional modes, since to observe emission bands there must be a considerable number of molecules in the excited state at the operational temperature and torsional modes are often the lowest vibrational modes in the molecule. This method can thus be applied to the determination of barrier heights in the same way as in torsional studies by far infrared.

10. <u>Electronic Spectroscopy</u> Visible and ultraviolet absorption occurs when an electron is promoted to a higher electronic level. It is unusual for two conformers to absorb at sufficiently different wave numbers to be able to distinguish between them. However, conformers may absorb with sufficiently different intensity to make a distinction. This method depends upon the establishment of limits of extinction coefficient from molecules fixed in one conformation in cyclic or sterically hindered compounds and comparison with extinction coefficients in labile systems.

11. Optical Rotatory Dispersion and Circular Dichroism Optical activity is caused by differences in the speed between right and left circularly polarised light which results in rotation of the plane of polarisation. It is observed in molecules which are asymmetrical. Optical rotatory dispersion (ORD) involves the study of optical activity with changes in wavelength. ORD curves may show maxima and minima close to an absorption due to an electronic transition.

- 9 -

This phenomena is known as the Cotton effect. The extinction coefficients of right and left circularly polarised light may differ near an absorption band. This difference is known as circular dichroism (CD). Both ORD and CD studies are difficult to interpret unless conformational studies by these techniques have been understood for related molecules. It is important to note that molecules with inherently dissymmetric chromophores, (usually two conjugated chromophores twisted at an angle to one another such as skewed dienes) give rise to Cotton effects in ORD curves and this effect can be used to study planarity of conjugated systems. 12. Rotational Spectroscopy The microwave spectrum of a molecule is obtained in the gaseous state as a set of very sharp lines. These sharp lines correspond to absorption of electromagnetic radiation corresponding to transitions between the rotational energy levels of the molecule. Rotational energy levels are dependent on the moments of inertia of the molecule. These levels are complex in a molecule where all the three moments of inertia are different. From a microwave spectrum these moments of inertia can be calculated. In some cases all the lines present cannot be explained in terms of one set of moments of inertia and in these cases more than one conformer must be present. In order to obtain molecular parameters. it is necessary to use a series of isotopically substituted molecules and assume that angles and distances are unchanged on substitution. Thus ²H and ¹³C are used to determine interatomic distances and angles. It is difficult, even so, to determine actual distances and angles for molecules with a large number of atoms because only three moments of inertia can be calculated from each isotopically

- 10 -

different molecule. Information on the enthalpy difference can be obtained from the intensity of the lines as they vary with temperature as will be discussed for infrared bands. Information on the energy barrier to rotation can be obtained from the splitting of rotational levels which is caused by quantum mechanical tunnelling effects. (Rotational Raman can provide the same information as microwave studies. However, different selection rules operate and the technique is more difficult and has been little used).

13. Nuclear Magnetic Resonance Nuclear magnetic resonance involves transitions between different nuclear spin states in the presence of an applied field. Particular nuclei (most commonly 'H) absorb energy at different radiofrequencies when in different chemical environments owing to different amounts of shielding. Nuclear magnetic resonance experiments require a relative long time scale compared with other spectroscopic techniques. Thus the rate of interconversion of two conformers becomes important. The other important factors are the chemical shift differences and coupling constants between the resonances from nuclei in different environments. If rotation about a single bond is slow, two sets of resonances corresponding to the two different environments are observed. If the rotation rate is fast then a single set of absorption bands is obtained representing the average position of the nuclei. At intermediate rates. the absorption lines are broad as they begin to coalesce. By varying the temperature, the rate of reaction can be changed. Thus in theory, a temperature can be found at which the two

separate spectra for the two conformers coalesce into one. From the variable temperature measurements, barriers to rotation can be calculated and from the relative peak areas of the two forms, as observed in the spectra, the enthalpy difference can be determined. It is often not possible to reach a low enough temperature to observe two separate spectra. However, calculations of the relative amounts of the two conformers can still be made assuming the resonance positions of the individual conformers and also no intrinsic changes occur with change of temperature.

14. <u>Vibrational Spectroscopy</u> Infrared and Raman spectroscopy is concerned with transitions between different vibrational levels. Gaseous infrared studies show rotational fine structure and rotational band contours superimposed upon the band due to a vibrational transition. The rotational fine structure and the overall contour can be related to moments of inertia and conformations. Problems arise because of Coriolis interactions. These interactions can be large in highly symmetrical molecules and give rise to different rotational constants for different bands. However, in asymmetric top molecules, these effects are small and may be ignored.

For a single conformer 3N-6 fundamental modes of vibrations are expected at various frequencies (where N is the number of atoms in the molecule). Most of these can normally be observed by combined use of infrared and Raman techniques which provide complementary information since the observed spectra are governed by different selection rules.

- 12 -

Although many of the corresponding fundamental vibrations of different conformers are observed at the same frequency, those vibrations involving atoms in distinctly different environments often occur at different frequencies. Differences in molecular geometry may cause differences in the electronic character and hence force constants of bonds. These differences lead to changes in the character and frequency of certain modes. It is not always possible to relate observed differences in band frequencies and intensities to particular effects, but this does not impair the importance of empirically established regularities in their application to conformational analysis. From temperature variation, values of the enthalpy differences and in some cases entropy difference can be calculated.

Torsional frequencies have been used to determine barriers to rotation about single bonds. The value of the torsional frequency may be related to the height of the barrier to rotation.

C THE CONFORMERS OF A 9 -UNSATURATED CARBONYL COMPOUNDS AND RELATED COMPOUNDS

The first attempt to establish the position of equilibrium between the two planar conformers in conjugated systems as represented by butadiene, acraldehyde and glyoxal was that of Mulliken⁴ who concluded that a conformation which he designated⁵ <u>s-trans</u> predominated over the other conformer which he designated <u>s-cis</u> for butadiene.





- 13 -

For the purposes of this work, the designation <u>s-cis</u> is used to include possible non-planar forms approaching the <u>s-cis</u> planar conformation.

Dipole moments were first used to establish the conformation of open chain \mathcal{A}^{3} -unsaturated carbonyl compounds. From these studies, Sutton and coworkers⁶ concluded that aeraldehyde $(CH_{2}=CH-CHO)$ and <u>trans</u>-crotonaldehyde $(CH_{3}CH=CH-CHO)$ were present in the <u>s-trans</u> conformation and mesityl oxide $((CH_{3})_{2}C=CHCOCH_{3})$ in the <u>s-cis</u> conformation. They were less certain about other compounds such as methacraldehyde $(CH_{2}=C(CH_{3})CHO)$. Electron diffraction studies⁷ suggested mixtures of 3:1 <u>s-trans:s-cis</u> at room temperature for acraldehyde and equal amounts of <u>s-trans</u> and <u>s-cis</u> at 70⁰ in crotonaldehyde.

Acraldehyde⁸ and its isotopically substituted species⁹ have been examined by microwave and no evidence has been found for an isomer other than the <u>s-trans</u> form. Ultrasonic studies¹⁰ show evidence for an overwhelming proportion of the <u>s-trans</u> form whereas Molar Kerr constants¹¹ favour a 4:1 <u>s-trans:s-cis</u> ratio. A recent variable temperature N.M.R. study¹² was fairly inconclusive although a variable temperature infrared study¹³ suggested there was evidence of a small amount of <u>s-cis</u> based on very weak shoulders on bands at 630 cm⁻¹ and 1 100 cm⁻¹.

Studies of crotonaldehyde have also reached the conclusion that all or most of the molecules are in the <u>s-trans</u> conformations; namely 96% <u>s-trans</u> from Molar Kerr constants¹¹ and virtually all <u>s-trans</u> from ultrasonic measurements¹⁰ and ultraviolet absorption measurements¹⁴.

- 14 ---

Other aldehydes have been found to exist in equilibrium mixtures. For example although an averaged spectra is observed at room temperature, at temperatures below -80° the interconversion of <u>s-trans</u> and <u>s-cis</u> conformers of 2-furanaldehyde is sufficiently slow for two separate signals to be observed for the aldehydic hydrogen and one of the ring protons¹⁵. The approximate enthalpy difference was calculated to be 1.0 Kcal mol⁻¹ (4.2 KJ mol⁻¹). Two separate carbonyl absorptions at 1 686 cm⁻¹ and 1 710 cm⁻¹ have been observed in the infrared¹⁶ for 2-furanaldehyde.

Mecke and Noack^{17,18} have shown that the conformations of A3-unsaturated carbonyl compounds can be distinguished by the positions and intensities of the C=C and C=C stretching frequencies in the infrared. From variable temperature infrared and Raman studies, Noack and Jones¹⁹ were able to show that methyl vinyl ketone (CH2=CH-COCH2) and ethylideneacetone (CH₃CH=CH-COCH₃) were present in an equilibrium mixture in which the s-trans conformations were more stable at room temperature in solution and were present exclusively in the crystalline solid. For example, in ethylideneacetone, using a eutectic solvent containing CHCl₃, CCl₄ and C₂Cl₄, bands were observed at 1 674 and 1 645 cm⁻¹ assigned to the <u>s-trans</u> conformer which increased in intensity relative to bands at 1 693 and 1 630 cm⁻¹, assigned to the s-cis conformer, as the temperature was lowered. Microwave studies²⁰ failed to show any evidence for an equilibrium in methyl vinyl ketone and only the s-trans form was detected. However, these measurements were carried out at -78° and the relative amount of s-cis would be small at that temperature. A recent variable temperature N.M.R. study²¹ of methyl vinyl

ketone and ethylideneacetone, although not conclusive supports the evidence that an equilibrium mixture is present. The infrared spectral studies of Kossanyi²² on alkyl vinyl ketones CH_=CH-CO-R suggested that for large alkyl groups, the s-cis conformation was favoured. ORD²³ and CD studies²⁴ have been carried out on grouping is a symmetric chromophore and shows Cotton effects only in the presence of an asymmetric centre. However, if the chromophore is non-planar, then larger Cotton effects are observed because the conjugated grouping has become an inherently dissymetric chromophore. From Molar Kerr constants²⁵ mesityl oxide is thought to be in a non planar s-cis conformation. From Molar Kerr constants²⁶ methyl acrylate was thought to be s-trans, cis with the methyl ester group twisted out of the plane. This was in reasonable agreement with an earlier electron diffraction study²⁷.

Various acid halides have been examined. From infrared spectra, acryloyl chloride and bromide²⁸ exist in an equilibrium mixture. This also seems to be true in crotonyl chloride²⁸. Microwave²⁹ and infrared³⁰ studies suggested there is little difference in enthalpy between the <u>s-cis</u> and <u>s-trans</u> forms of acryloyl fluoride. N.M.R. studies³¹ give a larger enthalpy difference between the two forms and the more stable form is considered to be the <u>s-trans</u> conformer. However, an average spectra is observed down to -95° and the method is, therefore, less accurate. Two forms have been detected from a ¹⁹F N.M.R. study of the completely fluorinated acraldehyde species³². A microwave study³³ of acrylic acid also suggests comparable proportions of the two conformers. It is interesting to note that 2-furanaldehyde, 2-acetylfuran and methyl 2-furanoate all show evidence of two carbonyl bands in the infrared and these are assigned to the s-cis and s-trans forms¹⁶.

Since unsaturated esters can show rotational isomerism other than the s-trans, s-cis type, a discussion of possible conformations of saturated esters is appropriate. The ester grouping can exist in two planar forms known as cis and trans.



cis

Microwave³⁴ and infrared³⁵ studies suggest that methyl formate exists in the cis conformation. The same conformation is believed to be present in methyl acetate from electron diffraction studies³⁶. The only type of esters thought to have the trans conformation are various fluoroformates where the evidence is based on N.M.R. and dipole moment studies 57.

 R^1

An additional conformational isomerism has been suggested in ethyl formate from microwave studies 38.



trans

trans



A similar equilibrium has been used to explain the variation of 13 C-H coupling constants with temperature in a series of alkyl acetates³⁹. The presence of different conformers due to rotation about the C-C (Carbonyl) has also been suggested in monochloro-acetate esters on the basis of two carbonyl absorptions in the infrared⁴⁰.



cis



staggered

Two similar conformers have been detected for propionaldeh is from microwave evidence. Thus the situation is complicated by the possibility of several conformers in both the saturated and unsaturated esters.

D THE CALCULATION OF THERMODYNAMIC FUNCTIONS

The relative stabilities of conformers may be expressed in quantitative terms by the application of thermodynamic concepts, enthalpy difference (Δ H), Gibbs free energy difference (Δ G), and the entropy difference (Δ S). From spectroscopic studies, all these thermodynamic functions are in principle determinable, however, it is important to be aware of the assumptions and limitations of these methods. The basis of the determination of thermodynamic functions from vibrational spectra will be outlined. The determination of the enthalpy is dependent on the van't Hoff isochore. The derivation of this is of some relevance to the significance of the result obtained.

Consider a reaction of the type

The expression for the change in free energy for this reaction is

$$\Delta G = \Delta G^{\circ} + RTln\left(\frac{a_{B}}{a_{A}}\right)$$
(1)

where ΔG° is the standard free energy change, a_{A} and a_{B} are the activities of A and B respectively for the particular stage at which the reaction is considered. There are two special cases which may be considered.

1) If the reaction is at equilibrium

$$\frac{a_{\rm B}}{a_{\rm A}} = K_{\rm a} \bigtriangleup G=0$$

Hence $\Delta G^{\circ} = -RTlnK_{u}$

2) If the reactants and products are in their standard states $(a_A = a_B = 1)$

$$\Delta G = \Delta G^{\circ} = -RT \ln K_{\rho}$$
(3)

(2)

Hence equation (3) gives the difference in free energy between the products in their standard states and the reactants in their standard states.

For a gaseous reaction at constant pressure, the standard state may be taken to be one atmosphere pressure.

$$\Delta G^{o} = -RTlnK_{p} \qquad (4)$$

$$K_{p} = \frac{v_{B}}{p_{A}} \qquad (5)$$

where p_A and p_B are the pressures of A and B respectively. Equation (4) can be differentiated with respect to temperature at constant pressure.

$$d\left(\frac{\Delta G^{\circ}}{dT}\right)_{p} = -RlnK_{p} - RT \frac{d}{dt} (lnK_{p})$$

This expression may be substituted in the Gibbs Helmholtz equation.

$$\operatorname{Td}\left(\frac{\Delta G^{\circ}}{\mathrm{dT}}\right)_{p} = \Delta G^{\circ} - \Delta H^{\circ} \qquad (6)$$

to give

$$\frac{d(\ln K_p)}{dT} = -\frac{\Delta H^0}{RT^2}$$
(7)

where ΔH° is the difference in enthalpy between products and reactants in their standard states. The difference between ΔH° and ΔH (difference in enthalpy between products in any general state) is dependent on the variation of activity coefficient with temperature and is usually small.

Equation (7) can be integrated.

$$\ln K_{\rm p} = \frac{\Lambda {\rm H}^{\rm o}}{{\rm RT}} + {\rm c}$$
 (8)

The value of the integration constant can be obtained from the relationship.

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$
 (9)

Comparison with equation (2) leads to the expression

$$\ln K_{\rm p} = -\frac{\Lambda {\rm H}^{\rm o}}{{\rm RT}} + \frac{\Lambda {\rm S}^{\rm o}}{{\rm R}}$$
(10)

Thus the integration constant in (8) is $\Delta S^{\circ}/R$. If ΔH° and ΔS° are independent of temperature, than a graph of ln K_p against 1/T has a slope of $-\Delta H^{\circ}/R$ and an intercept at 1/T=0 of $\Delta S^{\circ}/R$. If ΔE° and ΔS° are temperature dependent, then a tangent to the above graph has a slope of $\Delta H^{\circ}/R$ and intercept $\Delta S^{\circ}/R$. Similar results are obtained from graphs of ln K_a against 1/T in solution.

If the intensity of absorption bands assigned to the reaction components A and B in either the gaseous or condensed state are measured at a sories of temperatures, the value of ΔH° can be calculated⁴².

For the reaction

A com B

Pressure or concentration $c_A = c_B$ Absorbance $A_A = A_B$ (for a selected band) Extinction Coefficient $\mathcal{E}_A + \mathcal{E}_B$ (for a selected band) From the Beer-Lembert Law

$$K = \frac{o_B}{c_A} = \frac{\varepsilon_A A_B}{\varepsilon_B A_A}$$
(11)

Substitution of equation (11) in equation (10) leads to the expression

$$\ln\left(\frac{A_{\rm B}}{A_{\rm A}}\right) = -\frac{\Delta {\rm H}^{\rm o}}{{\rm RT}} + \frac{\Delta {\rm S}^{\rm o}}{{\rm R}} + \ln\left(\frac{{\cal E}_{\rm A}}{{\cal E}_{\rm B}}\right) \qquad 1(12)$$

If it is assumed that the ratio ($\mathcal{E}_A/\mathcal{E}_B$) is invariant with temperature the value of ΔH^0 may be obtained from a graph of $\ln(\Lambda_B/\Lambda_A)$ against $1/T^0K$. The absorbances can either be measured from peak heights, or where there is little overlap, from peak areas.

 ΔS° cannot readily be obtained from this method since the intercept is dependent on both ΔS° and the ratio of the extinction coefficients. Two different procedures have been used for the determination of ΔS° . Further assumptions or restrictions in applicability are involved in both methods. The common band method of Mizushima⁴³ assumes that the extinction coefficient of a common band (\mathcal{E}_{\circ}) is the same for the two different conformers and all the extinction coefficients vary in the same way with temperature.

$$\frac{\ln\left(\frac{o_{B}}{o_{A}}\right)}{\frac{o_{B}}{c_{A}}} = -\frac{\Delta H^{o}}{RT} + \frac{\Delta S^{o}}{R}$$
(13)
$$-\Delta H^{o}/RT \quad \Delta S^{o}/R$$
$$\frac{o_{B}}{c_{A}} = e \quad e$$

$$\frac{c_A}{c_A + c_B} = \frac{1}{1 + c_B / c_A} = \frac{1}{1 + e^{-\Delta H} / RT} + \frac{1}{e^{-\Delta H} / RT}$$

But

Thus

$$\frac{c_{A}}{c_{A}+c_{B}} = \frac{A_{A} \mathcal{E}_{c}}{\mathcal{E}_{A} A_{c}}$$

 $\frac{A_{A} \mathcal{E}_{O}}{\mathcal{E}_{A} A_{O}} = \frac{1}{1 + e^{-\Delta H^{0}/RT} e^{\Delta S^{0}/R}}$ $e^{-\Delta H^{0}/RT} e^{\Delta S^{0}/R} = \frac{\mathcal{E}_{A} A_{O}}{\mathcal{E}_{O} A_{A}} = 1$

(14)

The unknowns in this equation (14) are ΔS° and $\mathcal{E}_{A}/\mathcal{E}_{B}^{\circ}$. By studying the ratio of the absorbances of a band from one conformersand a common band, for, at least, two temperatures, ΔS° can be evaluated by solving two simultaneous equations in two unknowns.

The second method⁴⁴ involves the further assumption that each extinction coefficient, (\mathcal{E}_A and \mathcal{E}_B), is independent of temperature. Thus if the total concentration of the two conformers is c_m

Then

$$c_{T} = o_{A} + c_{B}$$

$$c_{T} = \frac{A_{A}}{\varepsilon_{A}L} + \frac{\Lambda_{B}}{\varepsilon_{B}L}$$
(15)

On rearrangement

$$A_{A} = -\epsilon_{A}A_{B} + \epsilon_{A}c_{T}$$
(16)

Hence a graph of A_A against A_B at different temperatures gives a straight line plot with a slope equal to $-(\mathcal{E}_A/\mathcal{E}_B)$. Hence ΔG° may be obtained from the expression $\Delta G^{\circ} = -RT(\ln K) = -R$

Other assumptions have been made to determine the free energy and entropy of conformational equilibrium, namely that the extinction coefficients are equal, that the extinction coefficients of closely related molecules can be transferred,

that the internal entropy difference is zero. All these methods have their deficiencies 44. Extinction coefficients vary greatly from one molecule to another. It has been shown that the extinction coefficient of the C-Cl stretching vibration in 4 tertiary-butyl-cyclohexyl chloride is one and a half times greater in the equatorial conformer than in the axial conformer⁴⁵. A vibration is not normally localised and changes in conformation are likely to affect both frequency and intensity. Assumptions that the internal entropy of different conformers is the same are clearly inaccurate. The rotational and vibrational contributions to the entropy are different for two conformers unless the moments of inertia are the same and all the low lying molecular vibrations such as torsion and skeletal modes occur at the same wave number. It would be useful to obtain entropy values since a higher entropy would be observed for a non-planar form because at least two conformers of the same energy would be possible.

It is clear that the accuracy of any value of a thermodynamic function depends upon the validity of the assumptions made. The precision of the value depends upon the magnitude of the errors in the experimental measurements. The significance of the results obtained in the present work must be considered in these contexts.

- 24 -

CHAPTER II

EXPERIMENTAL

- A Purification of Compounds
- B Vibrational Spectroscopy
 - C N.M.R. Spectroscopy
 - D Mass Spectroscopy

A PURIFICATION OF COMPOUNDS

<u>Acraldehyde</u> (B.P. Chemicals Ltd.) was purified by distillation under nitrogen in subdued lighting. The azeotropic mixture boiling at 52° was collected and water removed with molecular sieve (3A).

<u>Crotonaldehyde</u> (Hopkin and Williams Ltd) was distilled under nitrogen using a twelve inch column packed with glass helices, collecting the fraction boiling between $102 - 103^{\circ}$. Other samples of crotonaldehyde were purified using preparative chromatography with an SE 30 column.

The following materials were prepared by distillation at atmospheric pressure using a fractionating column and the fractions were collected in the range indicated:

Methyl vinyl ketone (Kodak Ltd.)	79 - 80 ⁰
Methyl acrylate (B.D.H. Ltd.)	80 - 81 ⁰
Ethyl acrylate (B.D.H. Ltd.)	99 - 100 ⁰
Methyl trans-crotonate (B.D.H. Ltd.)	120 - 121 ⁰

Preparative gas chromatography was used to prepare ethylideneacetone and ethyl <u>trans</u>-crotonate. A Varian Aerograph Autoprep 705 instrument was used.

<u>Ethylideneacetone</u> (B.P. Chemicals Ltd.) supplied as a mixture containing ethylideneacetone as its major component was partly purified using a Carbowax 20M column. Further purification was achieved using an SE 30 column.

Ethyl trans-crotonate (Koch Light Ltd.) was purified using a Carbowax 20M column.

- 26 -

All the samples were stored below 0° , dried using molecular sieve(3A) and the purities checked by gas chromatography using a Varian Aerograph 660 or a Phillipps PV 400. Purities were checked using a polar Carbowax column and a non-polar SE 30 column. The aldehydes were found to be air sensitive when pure, tending to oxidise and polymerise, and for this reason were stored under nitrogen.

A number of other esters were used for comparison. These were either commercially available or were prepared by esterification of the appropriate organic acid in the presence of a small quantity of strong acid. Preparative gas chromatography was used to obtain pure samples of the esters prepared in this way. TABLE I Compounds whose spectra were examined in detail

Compound	Structure (in <u>s-trans</u> form)	Discussion of important spectra	
Acraldehyde	H = C = C $H = C = 0$	Infrared Resolved Fine Structure p 43 Infrared Variable Temperature Studies p 54 Vibrational Assignments p 83 Nuclear Magnetic Resonance Spectra p 130 Mass Spectra p 148	
<u>Trans-</u> Crotonaldehyde	$CH_{3} C = C H_{1} C = 0$	Infrared Resolved Fine Structure p 49 Infrared Variable Temperature Studies p 54 Vibrational Assignments p 83 Nuclear Magnetic Resonance Spectra p 130 Mass Spectra p 148	
Methyl vinyl ketone	$H = C = C = 0$ CH_3	Infrared Band Contours p 51 Infrared Variable temperature Studies p 54 Vibrational Assignments p 83 Nuclear Magnetic Resonance Spectra p 138 Mass Spectra p 148	
Ethylideneacetone	$CH_{3} = C = C$ $H = C$ $CH_{3} = 0$	Infrared Variable Temperature Studies p 61 Vibrational Assignments p 83 Nuclear Magnetic Resonance Spectra p 140 Mass Spectra p 148	
TABLE	I	(Cont	t:
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Continued)

Compound	Structure (in <u>s-trans</u> form)	Discussion of important spectra
Methyl acrylate	$H = C = C = 0$ CH_{3}	Infrared Band Contours p 51 Infrared Variable Temperature Studies p 67 Vibrational Assignments p 83 Nuclear Magnetic Resonance Spectra p 140 Mass Spectra p 153
Ethyl acrylate	$H = C = C = 0$ $C = 0$ $C_2 H_5$	Infrared Band Contours p 53 Infrared Variable Temperature Studies p67 Vibrational Assignments p 83 Nuclear Magnetic Resonance Spectra p 143 Mass Spectra p 153
Methyl <u>trans</u> -crotonate	$CH_{3} C = C H_{1} C = 0$ $CH_{3} C = C$	Infrared Variable Temperature Studies p 64 Vibrational Assignments p83 Nuclear Magnetic Resonance Spectra p 140 Mass Spectra p 153
Ethyl trans-crotonate	$CH_{3} = C_{1} = C_{1}$ $H_{1} = C_{2} = 0$ $C_{2}H_{5}$	Infrared Variable Temperature Studies p 67 Vibrational Assignments p 83 Nuclear Magnetic Resonance Spectra p 143 Mass Spectra p 153

- 29 -

B VIBRATIONAL SPECTROSCOPY

Spectra were recorded using several different instruments. Standard spectra as thin films, solutions in carbon tetrachloride and vapour were recorded at room temperature on a Perkin-Elmer 457 grating infrared spectrophotometer having a spectral band width of about 2 cm⁻¹ in the range 4 000 to 400 cm⁻¹ and a wavenumber accuracy of 2 - 3 cm⁻¹ depending on the region of the spectra. All wavenumber measurements were calibrated⁴⁶ using indene for standard spectra and ammonia and water vapour for expanded vapour spectra. Standard cells were used with KBr windows.

The variable temperature intensity measurements were made on a Grubb Parsons Spectromaster for which the transmission scale was calibrated before each set of measurements by high speed sectors of standard 20% and 50% transmission. The accuracy was found to be + 1% of peak absorbance in terms of absorbance units. The cells and associated equipment for variable temperature studies were supplied by R.I.I.C. For solution studies the VIT2 unit was used with silver chloride and KRS5 cell windcws. The latter caused strong interference fringes even with filled cells because of the high refractive index of this material. However, the difficulties caused by the interference fringes were reduced by using cells of 1 mm thickness instead of 0.1 mm. The cell unit could be heated electrically and cooled using a refrigerant. A solid carbon dioxide/acetone mixture was used for temperatures down to -70°. Below this temperature nitrogen was used down to -170°. It was found to be more difficult to maintain a steady temperature over a relatively long period using liquid nitrogen. A low vacuum was

- 30 -

used to limit formation of ice crystals on the inner cell windows. A high vacuum tended to cause leakage from the cell. Variable temperature solution studies were normally carried out in carbon disulphide. For vapour studies, the GH7 truncated cone heated gas cell was used with KBr windows. The cell was evacuated and samples admitted either through a silicone rubber septum from a syringe or on a vacuum line. The temperature within the cells were measured by a sheathed iron constantan thermocouple for which a potentiometer was calibrated using the boiling point and freezing of water, the liquid temperature of a CO_2 /ether freezing mixture (-78.3°) and for intermediate temperatures the readings of mercury and alcohol thermometers. The temperature was maintained within a 2° range during absorbance measurements. Initially solution intensities were obtained at room temperature and compared with intensities at -70° using carbon dioxide/acetone coolant. Certain bands were then studied at temperatures between -110° and 40° in solution and temperatures between 20° and 200° in the vapour. Peak height measurements were made at 10 - 15 values of temperature, in duplicate. Band area measurements were also made where possible by replotting bands recorded at slow scan speeds (12 cm⁻¹ per Min) in absorbance units and summing the area under the band by taking the mean of three planimeter readings in arbitary units.

Certain infrared vapour bands were recorded on a Perkin-Elmer 521 (Chester Beatty Research Institute, Fulham) and a Unicam SP 100 (B.P. Chemicals Ltd., Epsom). These instruments have a spectral band-width of better than 1 cm⁻¹ under expanded scale conditions where the wavenumber accuracy is approximately 0.5 cm⁻¹.

- 31 -

Raman spectra were recorded for the $\partial \beta$ -unsaturated esters on a Carey 81 Laser Raman instrument (Imperial College, London). This incorporates the Spectro-Physics He/Ne gas laser as a Raman source, emitting radiation at 15 797.8 cm⁻¹ with a power of 90 - 100 mW. The spectra are accurate to about 2 cm⁻¹ in all ranges.

C NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance studies were carried out using a Perkin-Elmer RIO 60 mHz instrument with a thermostatted permanent magnet. The resolution is better than 0.5 Hz and the field drift during the recording of a spectra less than 1 Hz. The Perkin-Elmer variable temperature probe was used with liquid nitrogen as coolant. In the early stages, a Varian A60 instrument (Varian Ltd., Walton-on-Thames) with an electromagnet was used.

D MASS SPECTROSCOPY

Mass spectra were recorded using an A.E.I. MS2 mass spectrometer with a multichannel galvanometer detector operating at an electron beam energy of 70 eV. The samples were injected using a gallium inlet system at a temperature of 100° . Source pressures were in the range $4 - 9 \ge 10^{-7}$ mm of Hg. Care was required as the samples were likely to polymerise during injection. Improved metastables results were obtained from mass spectra recorded on an A.E.I. MS9 mass spectrometer, (School of Pharmacy, London).

Certain computer programmes (see Appendix I) were written in the AIGOL 60 programming language and run on the Elliott 4120 computer with a 4298 digital incremental plotter using punched paper tapes.

- 32 -

CHAPTER III

VIBRATIONAL SPECTROSCOPY

A Rotational Fine Structure and Contours of Infrared Bands in the Vapour State.

B Variable Temperature Infrared Measurements.

C Assignment of Bands.

A ROTATIONAL FINE STRUCTURE AND CONTOURS OF INFRARED BANDS IN THE VAPOUR STATE

In the gaseous state, vibrational absorption bands show rotational fine structure or a characteristic outline contour. These features are caused by changes in the rotational levels. which can accompany changes in the vibrational level. A vibration-rotation absorption band may be resolved into rotational fine structure, if the resolving power of the spectrometer is sufficient to separate the individual rotational sub-bands; an outline band contour will be observed if the spectrometer cannot resolve these sub-bands. The separation between sub-bands due to rotational changes is large if the values of the moments of inertia about the principal axes are small. These axes are the mutually perpendicular axes about which the moments of inertia have minimum, intermediate, and maximum values and are termed the A, B and C axes respectively. The moments of inertia can be calculated about any three mutually perpendicular axes knowing the masses of the atoms, internuclear distances and bond angles. These can be converted into principal moments of inertia by a simple mathematical procedure 47 when the molecule has an effective plane of symmetry, since the maximum value of the moment of inertia is fixed about an axis perpendicular to the plane of the molecule. The molecules studied have been treated as effectively planar molecules.

Molecules can be classified according to the values of three principal moments of inertia. In the present work all molecules are treated as approximate prolate symmetric rotors. This is because the moments of inertia about the B and C axes are approximately equal and much larger than the moment of inertia about the A axis. This approximation is reasonable for the <u>s-trans</u> conformation of acraldehyde but is less valid for certain others, particularly the <u>s-trans</u> form of methyl vinyl ketone.

1. Resolved Fine Structure - Rotational Sub-Bands

The rotational fine structure of a band in a prolate symmetric top depends upon the direction of the oscillating dipole associated with the vibration. Different structure is observed for vibrations with oscillating dipoles parallel to the A, B or C principal axes since different selection rules operate. The total energy E(V,R) of a vibration-rotation level in an asymmetric top which approximates to a prolate symmetric top is given by⁴⁸

$$E(V,R) = E_{v} + (\frac{B+C}{2}) J(J+1) + (A - \frac{B+C}{2})K^{2}$$
 (1)

where J and K are the rotational quantum numbers, E_v is the vibrational energy and A, B and C are the rotational constants given by $A = h/8\pi^2 I_A$, $B = h/8\pi^2 I_B$, $C = h/8\pi^2 I_0$ where I_A , I_B , I_C are the moments of inertia about the A, B and C ares respectively.

- 35 -

For a band parallel to the A axis, (Type-A bands) the selection rules are $\Delta J=0, \pm 1$; $\Delta K=0$; a central Q branch, and P and R branches of spacing (B+C) are observed. This corresponds to the parallel band of a symmetric top molecule. For bands parallel to the B axis (Type-B bands) the selection rules are $\Delta J=0, \pm 1$; $\Delta K=\pm1$; a series of Q branches are observed with separation $2(A=\frac{1}{2}(B+C))$. A central Q branch is not observed. For bands parallel to the C axis (Type-C bands) the selection rules are $\Delta J=0, \pm 1$; $\Delta K=0, \pm 1$; a series of C branches are observed with the same separation as a Type-B band. In this case, however, a strong central Q branch is observed. As the ratio of the rotational constants B/A decreases, a weaker Q branch is observed.

A more detailed expression for the position of the fine structure of a C-Type band for an approximate prolate top is given by

$$\mathcal{V}_{o}^{\text{sub}} = \mathcal{V}_{o}^{+} \left(A_{o}^{-} \left(\frac{B_{o}^{+}C_{o}}{2} \right) \right)^{+} 2 \left(A_{o}^{-} \left(\frac{B_{o}^{+}C_{o}}{2} \right) \right) \frac{K_{+}}{K_{o}^{+}} \left(A_{o}^{-} \left(\frac{B_{o}^{+}C_{o}}{2} \right) \right)^{-} \left(A_{1}^{-} \left(\frac{B_{1}^{+}C_{1}}{2} \right) \right)^{K_{o}^{+}}$$

$$(2)$$

where A_0 and A_1 are the rotational constants in the vibration states v = 0 and 1 respectively. The effective rotational constants for a vibrational energy level (v) are given by

$$A_{v} = A_{o} = \measuredangle_{A} (v + \frac{1}{2})$$
$$B_{v} = B_{o} = \measuredangle_{B} (v + \frac{1}{2})$$
$$C_{v} = C_{o} = \measuredangle_{C} (v + \frac{1}{2})$$

where y = 0, 1, 2.....

Different rotational constants may be observed in different vibrational energy levels. The \measuredangle term is made up of two main contributions. One of these contributions arises from the anharmonicity of vibrations. This results in the internuclear separation increasing in higher vibrational levels. The other contribution arises from Coriolis forces which occur in a moving particle. When a particle is moving, a force is directed at right angles to the direction of motion. This Coriolis force leads to changes in the combined vibrationrotation energy levels. Thus the pure rotational energy levels, observed when no vibration is occuring, are perturbed. This effect is small in molecules with low symmetry such as C_g symmetry. The expression (2) can be further complicated by allowing for centrifugal distortion which leads to higher terms in J and K.

The expression (3) is used if the accuracy of the data is such that it is only possible to fit the observed values of wavenumber to a linear equation in K. In this case, only average values of A, B and C for the two vibrational levels can be obtained.

$$A_{o} = A_{1} = A; \quad B_{o} = B_{1} = B; \quad C_{o} = C_{1} = C$$

$$\mathcal{V} \quad \sup_{o} = \mathcal{V}_{o} + \left(A - \left(\frac{B+C}{2}\right)\right) + 2\left(A - \left(\frac{B+C}{2}\right)\right) K \quad (3)$$

The sub-bands observed are labelled ${}^{R}Q_{K}$ and ${}^{P}Q_{K}$ corresponding to the transitions $\triangle K = +1$, $\triangle K = -1$, where K is the rotational quantum number of the lower vibrational level from which the transition occurs.

- 37 -

The fine structure of A and B-Type bands can be treated in a similar manner.

2. Unresolved Band Contours

In molecules where the moments of inertia are large, only a band contour is observed. Different contours are observed for bands caused by vibrations in which the oscillating dipole is parallel to the A, B or C principal axes. The A-band is observed to have PQR structure, the B-band PR structure and the C-band PQR structure with a pronounced Q band. These different types of bands are illustrated for molecules with moments of inertia with similar values to those in the molecules studied⁴⁹.

Parallel to A axis

Parallel to B axis

Parallel to C axis

The separation between the maxima of the P and R branches of a parallel band in a linear molecule can be obtained by application of the Maxwell Boltzmann law, allowing for the rotational degeneracy factor (2J+1).

$$\Delta v = \frac{1}{\pi} \int \frac{KT}{T}$$
 (4)

Gerhard and Dennison⁵⁰ have shown that the separation between the maxima of the P and R branches of a parallel band in a prolate symmetric top is given by (5) an extension of equation (4).

$$\Delta \nu = \frac{S(B)}{TT} \int \frac{KT}{I_c}$$
(5)

- 38 -

where $s(\beta)$ is given by the empirical formula

$$\log_{10} s(\beta) = 0.721$$
(6)
(β +4)^{1.13}

in which $\beta = A/C-1$.

Studies on asymmetric rotors were carried out by Badger and Zumwalt⁵¹. The contour could be represented in terms of two quantities $\rho = (A-C)/B$ and S = (2B-A-C)/(A-C). This work has recently been extended by Seth-Paul and Dijkstra⁵², and the PR separations are given in terms of somewhat different parameters (see Table 2.3). The contours and fine structure observed for various asymmetric top molecules have been illustrated for various values of A, B and C⁴⁹.

Calculations have been carried out to determine PR separations and rotational fine structure spacings for the aldehyde and ketone molecules, taking reasonable values for the bond lengths ($r_{o-o} = 0.146$ nm, $r_{o=o} = 0.136$ nm, $r_{c=o} = 0.121$ nm, $r_{o-Me} = 0.152$ nm, and $r_{C-H} = 0.109$ nm (alkene and alkane)), and assuming bond angles to be trigonal, planar or tetrahedral where appropriate. The moments of inertia were calculated and the direction of the A and B principal axes illustrated (Figure 1) for the planar <u>s-cis</u> and <u>s-trans</u> conformers using a computer program (Appendix I). The calculations were not carried out for the esters because little fine structure was observed. The calculated values are shown in Tables 2.3.

If the molecules under consideration are treated as planar molecules, all out-of-plane vibrations should be true



			Acralde	ehyde	Tra crotuna	ns- ldehyde	Methyl Ket	vinyl one	Ethyli acet	dene- one
		на се	<u>s-trans</u>	<u>s-7is</u>	<u>s-trans</u>	<u>s-cis</u>	s-trans	s-cis	<u>s-trans</u>	<u>s-cis</u>
Moments of inertia	IA		18.2	38 . 7	26.1	42.5	92.8	76.2	98.2	85.7
about the three	IB		177.6	126.0	374.9	308.5	187.3	210.8	423.1	44:5.7
principal axes (gm cm ² X 10 ⁴⁰)	r _c		195.8	164.6	395.6	345.7	275.8	281.8	510.7	520.8
Rotational	A		1.537	0.724	1.072	0.659	0.702	0.367	0.285	0.327
constants	В		0.158	0.222	0.0746	0.0907	0.149	0.133	0.0662	0.0628
(cm ⁻¹)	C		0.143	0.170	0.0708	0.0810	0.101	0.099	0.0548	0.0537
Spacing of rotatio	nal	sub-bands(cm)								
B & C type bands $2(A - \frac{B+C}{2})$			2.77	1.04	2.00	1.14	0.35	0.50	0.45	0.54
A type bands						n				
(B+C)	1 - 1 2 - 1		0.30	0.39	0.14	0.17	0.25	0.23	0.12	0.12

TABLE 2 Resolved Fine Structure Calculations

- 41 -

	Acraldehyde		<u>Trans</u> . crotonaldehyde		Methyl vinyl ketone		Ethylidene- acetone	
	s-trans	<u>s-cis</u>	s-trans	s-cis	s-trans	<u>s-cis</u>	s-trans	<u>s-ois</u>
S= <u>2B-A-C</u> A-C	-0.979	-0.819	-0.992	-0,966	-0.521	-0.750	-0.899	-0.933
$\rho = \frac{A-C}{B}$	8.82	2,50	13.43	6.37	1.34	2.02	3•47	4:35
$B = \frac{BC}{B+C}$.	0.075	●.096	0.036	0.043	0.060	0.057	, 0.030	0.029
$\overline{\beta} = \underline{\Lambda} - 1$	9•24	2.77	15.41,	7.18	1.52	2.23	4.00	4.98
S (B) where	1.09	1,21	1.06	1412	1;27	1.23	1.17	1,15
$\log_{10}S(\beta) = \frac{0.721}{27.01010}$								
$(3+4)^{2}$	1.568	1.774	1.092	1.185	1.414	1.367	0.993	0.977
(Δ⊽ PR	A band =	105(B) (m/9) ¹			<u>.</u>		
(AJ PR C	band =	3/2 07	PR A ban	d)	17.0	1/ 0	1 7 7 7	111 0
$\Delta \overline{v} A(cm^{-1})$	╡┷ <u>┎</u> ┪┷ ┶	21.07	LTO.	1707	1 - 1 - 7	10.0	11.0	1102
Avc(cm ^{PR} ·1)	25•7	32.3	17•4	20.0	26.9	25.2	17.4	16.8
If $\rho > 3$ $\triangle y PR$ band = 5/6 $\triangle \overline{y}$ PR A band								
$\frac{1}{4} \Delta \overline{\nu} PR band = (1/S(\beta))(\Delta \overline{\nu} PR A band)$								
AJ PR B(om ⁻¹)								
p>3	14.2	17.8	9-7.	11.1	14.1	13.7	9•7	9.3
P)			; , [

TABLE 3 Separation of P and R branches in the molecules studied according to the method of Seth-Paul et al.

C-Type bands. In-plane vibrations will only be accidentally A or B-Type bands and are more likely to be AB hybrid bands with the result that their structure will be rather indistinct.

Non-planar conformations are possible. These will be less likely to behave as approximate prolate symmetric tops. The minimum moment of inertia will be generally larger, depending on the dihedral angle about the $\alpha\beta$ C-C bond. Also all bands will only accidentally have dipole changes parallel to either A, B or C axes. Non-planar conformations would, therefore, not be expected to show bands with resolved fine structure with sub-bands having measurable separations, unless they have structures which are very close to truly planar forms. The observation of fine structure in out-of-plane vibrations in acraldehyde and <u>trans</u>-crotonaldehyde is itself supporting evidence for a planar molecule.

3. Results and Discussion

Only acraldelyde and <u>trans</u>-crotonaldelyde showed resolved fine structure, the other compounds revealed only band contours. a) <u>Resolved Fine Structure</u>

<u>Aoraldehyde</u> Bands centred at 592.9, 958.7 and 993.2 cm⁻¹ exhibited rotational fine structure with strong central Q bands (Figures 2,3). Assignments to the rotational sub-bands were made for the 593 cm⁻¹ band and for the non-overlapping wings of the 959 and 993 cm⁻¹ bands although it was difficult to assign the sub-bands close to the central maxima and in the region of overlap between 993 and 959 cm⁻¹ to the correct sub-bands (Table 4). These three vibrations have been assigned to the three out-of-plane modes associated with the vinyl





Assignments			<u>Trans-</u> Crotonaldehyde					
	∇	50	ν	5	Ū	50	Ū	22
^R Q16	640.2	2						
R _{Q15}	637.4	2.8						
R _{Q14}	63 4 . 8	2.6						
^R Q13	631.8	3.0						
^R Q12	629.0	2.8						
^R Q11	626.3	2•7						
R _{Q10}	623.6	2.7						
R _{Q9}	620.7	2.9						
^R Q8	618.0	2.7			1015.9		992•4	
^R Q7	615.0	3.0			1013.4.	215	990.2	2.2
RQ6	612.2	2.8			1010.9	2.5	988.2	2.0
R _{Q5}	609 .3	2.9			1008.0	2 . 9 ·	986.2	2.0
RQ4	606.5	2.8			1005.3	2.7	984.0	2.2
^R Q3	603.7	2.8			1002.6	2.7 -	981 . ''	2.3
R _{Q2}	601.2	2•5			(1001.1)	(1.5) ·	97)•7	2.0
R _{Q1}	598.4	2.8	•				977•3	2.4
R _{QO}	595.6	2.8	•					
Band Centre	592.9	2.7	958 •7		993.2		972•7	•
P _{Q1}	-	e.	(955.8)	(2.9)				
P _{Q2}	588.8		(953•7)	(2.1)			969.7	
P _Q 3	585.5	3.3	(951.9)	(1.8)	•			
P _{Q4}	582.3	3.3	949•2	2.7			965.8	•
PQ5	579.1	3.2	946•4	2.8			963.7	2.1
	ł						ана 19	

trans-crotonaldehyde (cm⁻¹)

- 47 -

TABLE 4 (continued)

Assignments			<u>Trans-</u> Crotonaldehyde					
	Ū	12	\overline{v}	5	$\overline{\nu}$	1	য	D2
P ₀₆	576.5	2.6	943.6	2.8			961.5	2.2
P.07	573.9	2.6	940.8	2.8			959.7	1.8
P _{Q8}	57049	3.0	938.1	2.7			957.6	2.1
P _{Q9}	528.0	2.9	935.2	2.9			955+7	1.9
P _{Q10}			932.6	·2.6			953.8	1.9
P _{Q11}		i	929•9	·2•7			951.7	2.1
P _{Q12}			927•3	· 2.6			949•8	1.9
P _{Q13}			924•4	2.9			948.0	1.8
P _{Q14}			922.0	2.4			946.0	2.0
P _{Q15}							944.0	2.0
Mean Separation		2.77		2.72	•	2,66	-	2.02

grouping by Potts and Nyquist⁵³. The nature of the 959 and 993 cm⁻¹ modes was thought to be as shown below.



For all three resolved vibrations, the sub-bands have been fitted to a linear equation in K rather than a quadratic involving K^2 terms. Hence the mean separations were calculated in each case and related to the mean rotational constant using equation (3). For these three modes, separations of the sub-bands of 2.77 cm⁻¹ were predicted for a C-Type band in the <u>s-trans</u> conformer and 1.04 cm⁻¹ for the <u>s-cis</u> conformer (Table 2). The separations observed were 2.77, 2.72 and 2.66 cm⁻¹ respectively (Table 4) which was in very close agreement with the calculated value for the <u>s-trans</u> conformer, but not for the <u>s-cis</u> conformer.

- Bands centred at 2 809, 2 759 and 2 700 cm⁻¹, whose assignment are shown, (Table 12) showed B-Type structure with rotational fine structure. The measured separations of the sub-bands was 2.81 cm⁻¹. Since these bands were associated with the C-H aldehydic stretching vibration, the separations observed suggested that the C-H stretching motion was approximately parallel to the B axis in the molecule in the <u>s-trans</u> conformation. Examination of Figure 1 showing the direction of the principal axes revealed that the aldehydic C-H bond was indeed parallel to the B axis in the <u>s-trans</u> conformation. Thus the evidence

- 48 -

suggested strongly that acraldehyde existed in the <u>s-trans</u> conformation.

<u>Trans-crotonaldehyde</u> A band centred at 972.7 cm⁻¹ in <u>trans-crotonaldehyde</u> showed resolved fine structure which was assigned to rotational sub-banus. (Figure 4 Table 4). No other bands showed fine structure.

This vibration was assigned by Potts and Nyquist⁵³ to the out-of-plane trans CH=CH twisting mode.



For an out-of-plane C-Type band, in <u>trans</u>-crotonaldehyde sub-band separations of 2.00 cm⁻¹ were predicted for the <u>s-trans</u> conformer and 1.14 cm⁻¹ for the <u>s-cis</u> conformer, (Table 2) using equation (3) and assuming average rotational constants. The observed sub-band separation was 2.02 cm⁻¹ (Table 4). This value was in very close agreement with the predicted spacing for the <u>s-trans</u> conformation but was in very poor agreement with the predicted spacing for the <u>s-cis</u> conformation. This appears to the first clearcut evidence that <u>trans</u>crotonaldehyde exists in the <u>s-trans</u> conformation.

In both acraldehyde and <u>trans</u>-crotonaldehyde, the accuracy of the sub-band separations was insufficient to obtain information on the different rotational constants in the vibrational energy states v = 0 and v = 1.



b) Band Contours

Band contours wore used as an aid in the assignment of vibrational modes where possible. In addition, the sharp nature of the strong central Q branch of C-Type bands was of considerable aid in distinguishing adjacent bands due to different conformations. This was especially true in methyl acrylate where little evidence could be obtained from solution studies.

Two out-of-plane vinyl modes were expected to occur in the 900 - 1 000 cm⁻¹ region of methyl vinyl ketone and methyl acrylate similar to the bands at 959 and 993 cm⁻¹ observed in aoraldehyde. In these molecules with large moments of inertia, no fine structure would be expected to be observed unless a spectrometer with very high resolving power was used (see Table 2 for ketones). However, these out-of-plane modes should have C-Type bands with a strong central maximum. This feature was of considerable importance in the interpretation of the spectra.

<u>Methyl Vinyl Ketone</u> and <u>Methyl Acrylate</u> In methyl vinyl ketone (Figure 5), three sharp maxima were observed at corresponding 1 002, 990 and 953 cm⁻¹ corresponding to the central Q branches of three bands. Since only two out-of-plane vibrations were expected, the appearance of three bands was thought to be associated with the existence of two or more conformers. In methyl acrylate (Figure 6), four sharp maxima were observed at 992, 987, 968 and 963 cm⁻¹ and these were assigned to the Q branches of four C-type bands arising from the presence of two

- 51 -



conformers. Similar observations and conclusions were made for ethyl acrylate. In both cases, the assignments are shown in the assignments section (Table 12, 13).

Contours of A, B and AB hybrid bands led to a considerable amount of overlap of most of the vibrational modes of the two conformers in the spectra of the compounds studied. Less information was therefore forthcoming from the vapour study of these bands than from vapour studies of C-Type bands.

In the solution state, bands which showed A, B or AB hybrid characteristics tended to become sharper and band overlap less marked. By contrast, C-Type bands became broader and band overlap more marked. Thus variable temperature studies and assignment of bands to different conformers required consideration of both vapour and solution spectra.

B VARIABLE TEMPERATURE INFRARED MEASUREMENTS

The effect of temperature variation on the infrared spectrum of a compound in the gaseous or solution state can aid the assignment of bands to a particular conformers in equilibrium. The experimental procedures for these studies have been described in Chapter IIB; the derivation of the thermodynamic functions of the equilibria have been discussed in Chapter I D.

It is important to note that, on cooling in solution, infrared bands usually increased in peak height, and the band width decreased. This cooling technique in general sharpened up shoulders on the side of other bands. Changes in intensity were noted relative to other bands in the spectrum. The initial measurements of intensity changes with temperature were based on peak heights in absorbance units. When there was little

- 53 -

overlap, area measurements could be carried out, measuring the peak areas using a planimeter. In practice, it was rare for no overlap to occur between bands in a spectrum, and often considerable overlap prevented the use of peak areas.

A computer program was used to calculate and plot $ln(A_1/A_2)$ against (1/T) and to draw a straight line based on the "least squares" method. A standard deviation was obtained using appropriate formulae for linear regression. The computer program is shown in Appendix I and the statistical analysis method discussed in Appendix II.

1. <u>AB-unsaturated Aldehydes</u>

Acraldehyde and <u>trans</u>-Crotonaldehyde No changes in intensity were observed with temperature in the infrared spectra of acraldehyde or <u>trans</u>-crotonaldehyde for the solution or vapour states despite recent evidence of small amount of a second conformer in acraldehyde¹³. It was concluded that acraldehyde and <u>trans</u>-crotonaldehyde molecules were essentially in one conformation and assignments were made on the basis of the <u>s-trans</u> conformation in Chapter III C.

2. AB-unsaturated Ketones

It has been noted¹⁹ that infrared and Raman spectra of methyl vinyl ketone and ethylidene acetone as liquids and solutions contained certain bands which weakened on heating (attributed to the <u>s-trans</u> conformer) and others shich intensified on heating (attributed to the <u>s-sis</u> conformer). <u>Methyl Vinyl Ketone</u> Three pairs of bands in methyl vinyl ketone have been investigated in detail (1 687 and 1 706 cm⁻¹, 1 246 and 1 180 cm⁻¹, 992 and 982 cm⁻¹; values in carbon disulphide solution). The assignments of these bands are given

in Table 12). Peak height calculations were made using carbon disulphide as solvent in the three regions stated. Values close to 400 cal mol⁻¹ (1.68 KJ mol⁻¹) were obtained (Table 6). Plots of the results as typical examples are shown in Figure 7 for the temperature range -110° to 40°. The close correspondence between the three values of ΔH° in the same solvent strongly supported the existence of a sirgle equilibrium between two forms. A study of the pair of carbonyl bands using pentane as solvent in the temperature range -90° to $+40^{\circ}$ produced a lower (14°) value of 338 ± 61 cal mol⁻¹ (1.41 ± 0.26 KJ mol⁻¹), which suggested the solvent effect might be significant but a very large number of careful measurements would be required to establish their significance and this aspect was not pursued. Because of the broad overlapping contours of the carboryl and vinyl twisting modes in the vapour, the only suitable pair of bands for variable temperature study in the vapour were those centred at 1 249 and \perp 189 cm⁻¹. ΔH° , calculated from peak height measurements over the temperature range 29° to 200°, was sound to be 600 \pm 60 cal mol⁻¹ (2.51 + 0.25 KJ mol⁻¹).

The large separation of the pair of bands near 1 250 and 1 180 cm⁻¹ and the lack of strong bands in the intervening region made the determination of ΔH° possible from band intensities using peak area measurements for both the solution in carbon disulphide and in the vapour state. A typical set of absorbance values of methyl vinyl ketone are presented (Table 5). Figure 9 shows the change in appearance of the spectrum at room temperature and -80° in carbon disulphide solution. The ΔE° values obtained were for carbon disulphide

- 55 -







TABLE 5 Typical Set of Absorbances obtained at various temperatures based on peak height measurements. (Measurements on C-C antisymmetric stretching vibration in methyl vinyl ketone in carbon disulphide solvent.

Temperature	<u>s-cis</u>	<u>s-trans</u>	$\ln\left(\frac{\text{cis}}{\text{trans}}\right)$	
Solution 1				
25.0	0,193	0.208	-0.072	
20.0	0.192	0.214	-0.105	
4.0	0.197	0.219	-0.105	
-10.0	0.204	€.258	-0.234	
-33.0	0 .204	0.283	-0.328	
-44.0	0.204	0.283	-0.328	
-56.0 '	0.203	0.280	-0.320	
-78.0	0.202	0.287	-0.352	
-89.0	0.203	0.354	-0.556	
-110.0	0.192	0.348	-0.595	
Solution 2				
35.0	0.200	0.220	-0.095	
25.0	0.195	0.215	-0.100	
20.0	0.197	0.222	-0,119	
4.0	0.189	0.217	-0.137	
-10.0	"0 . 191	0.236	-0.212	
-23.0	0.195	0.243	-0.222	
-33.0	0.198	0.265	-0.292	
-44.0	0.197	0.270	-0.304	
-55.0	0.199	0.292	0.384	
-89.0	0.202	0.343	-0.531	
-110.0	0.194	0.361	-0.620	

TABLE 6Enthalpy differences between s-cis and s-transconformers of methyl vinyl ketone

Vibrational Mode	State	Peak height or peak area	Wavenu value <u>s-cis</u>	mber1 (cm ¹) <u>s-trans</u>	Excess Enthalpy of <u>s-cis</u> conformer cal mol ⁻¹
Carbonyl stretch	Solution in CS ₂	P.H.	1706	1687	403 <u>+</u> 52
	Solution in n-pentane	P.H.	1706	1687	338 <u>+</u> 61
Vinyl out- of-plane twisting deformation	Solution in ^{CS} 2	P.H.	982	992	386 <u>+</u> 41
Skeletal C-C stretching	Solution in CS ₂	P•H•	1180	1246	428 ± 45 375 ± 38
vioration		P.A	1180	1246	461 <u>+</u> 23
	Vapour	P.H.	1180	1249	600 <u>+</u> 60
		P.A.	1180	1249	513 <u>+</u> 52

 $(-110^{\circ} to 40^{\circ}) 461 \pm 23 cal mol^{-1} (1.93 \pm 0.10 \text{ KJ mol}^{-1})$ and for the vapour (20° to 200°) 513 \pm 52 cal mol⁻¹ $(2.14 \pm 0.21 \text{ KJ mol}^{-1})$. Since band area measurements are less dependent on instrumental limitations such as finite slit width than peak height measurements, the results listed in Table 6 for peak area measurements were considered most reliable. Ethylideneacetone A similar study of ethylideneacetone using two pairs of bands (C=O stretch 1 674 and 1 692 cm⁻¹ and C-C skeletal mode 1 250 cm⁻¹ and 1 177 cm⁻¹) was made. (A third pair of bands was found to be temperature dependent (1 292 and 1 274 cm⁻¹ but further investigation was not carried out on this pair of bands). Similar results were obtained to those of methyl vinyl ketone. Mean ΔH^0 values obtained from peak height measurements for the two pairs of bands studied were 440 + 50 cal mol⁻¹ (1.84 + 0.21 KJ mol⁻¹) in solution in carbon disulphide in the temperature range -110° to $+40^{\circ}$. The individual values were 428 + 45 cal mol⁻¹ (1.79 + 0.19 KJ mol⁻¹) for the C=O stretching vibration and 460 ± 23 cal mol⁻¹ (1.93 + 0.10 KJ mol⁻¹) for the antisymmetric C-C stretching mode. Vapour studies were only carried out on the 1 252 and 1 177 cm⁻¹ pair of bands and a ΔH° value of 630 + 90 cal mol⁻¹ $(2.64 \pm 0.38 \text{ KJ mol}^{-1})$ was obtained for the temperature range 20° to 200°. Area measurements were carried out on the 1 250 and 1 177 cm⁻¹ pair of bands in solution and vapour. The change in appearance of the spectra at room and low temperature in solution is illustrated in Figure 10. The ΔH^{O} values obtained were 513 ± 52 cal mol⁻¹ (2.15 \pm 0.22 KJ mol⁻¹) for solution studies in the temperature range -110° to +40°, and

- 61 -



TABLE 7 Enthalpy differences $\triangle H^\circ$ of the conformers of ethylidene-acetone

Mode	Wavenum	ber (cm ⁻¹)	Excess enthalpy of <u>s-cis</u>	State	Peak height or peak
	<u>s-cis</u>	s-trans	cal mol ⁻¹		area
C=O stretch	1692	1674	· 428 <u>+</u> 45	Solution CS	P.H.
antisymmetric skeletal C-C	1177	1250	46 • ± 23	11	P.H.
stretch	1177	1250	513 <u>+</u> 52		P.A.
n an N aissian San San San San San San San San San S	1177	1252	630 <u>+</u> 90	Vapour	P.H.
U	1177	1252	585 <u>+</u> 46		P.A.

- 63 -

 585 ± 46 cal mol⁻¹ (2.45 \pm 0.19 KJ mol⁻¹) for the vapour in the temperature range 20° to 200° (Table 7).

In both methyl vinyl ketone and ethylideneacetone, the vapour $\triangle H^{O}$ values were larger than the solution values. This indicated that either the enthalpy difference was intrinsically larger in the vapour state or the $\triangle H^{O}$ was increasing with temperature. The second explanation seemed unlikely because the graphs did not show any noticeable curvature.

3. <u>AB-unsaturated Esters</u>

All the ΔH^{O} values for the $\Delta \beta$ -unsaturated esters are shown in Table 8.

<u>Methyl trans-Crotonate</u> Variable temperature studies of methyl <u>trans-crotonate</u> in solution in carbon disulphide revealed three pairs of bauds in the region between 1 350 and 1 150 cm⁻¹ which were temperature dependent. These are illustrated in Figure 11. In each of the pairs, the higher wavenumber band intensified as the carbon disulphide was cooled. The bands which showed temperature dependence occurred at 1 315 and 1 294 cm⁻¹, 1 275 and 1 268 cm⁻¹ and 1 196 and 1 178 cm⁻¹.

 ΔH° values from peak height measurements were calculated for the highest and lowest wavenumber pair of bands. The middle pair of bands was too closely overlapped to obtain an accurate value. The ΔH° differences obtained for the 1 315 and 1 294 cm⁻¹ pair were in good agreement with that of the 1 196 and 1 178 cm⁻¹ pair of bands. The ΔH° values obtained were 541 ± 34 cal mol⁻¹ (2.27 ± 0.14 KJ mol⁻¹) for the higher wavenumber pair and 509 ± 18 cal mol⁻¹

- 64 -


TABLE 8 Equilibrium measurements of enthalpy change between high and low energy forms of acrylates and <u>trans</u>-

crotonates.

Methyl and ethyl acrylate			Methyl	and ethyl .	trans-o	rotonate	
			, , , , , , , , , , , , , , , , , , , ,				A 110
Metnyl	∆H _	LTNYI	∆H	Metnyl		Etnyl	
om ⁻¹	cal mol ⁻¹	cm_1	cal mol ⁻¹	cm ⁻¹	cal mol-1	cm ⁻¹	cal mol ⁻¹
1290	x	1296	· x	1315	501 ± 32	1307	515 <u>+</u> 7C
1276		1271		1294		1294	
			•	1275	X	1275	x
				1268		1264	
1202	315 ± 45	1194	۰ ۲	1196	521 <u>+</u> 24	1184	x
1180		1170		1178		1174	
	(Measurem	ents of	solution i	n CS ₂ -1	10 ⁰ to +40 ⁶)	
992	Y	003	Y				
,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	A		^			<i>i</i>	•
987		988					
968	400 <u>+</u> 100	968	x				
963	-	96 3					• •
	(Measurem 20° t	ents of p 150°)	vapour		- -		·

X Meaningful measurements precluded by band overlap.

- 66 -

 $(2.13 + 0.07 \text{ KJ mol}^{-1})$ for the lower wavenumber pair in carbon disulphide solution in the temperature range -110° to +40°. Peak area measurements were carried out on both of these pairs of bands although the overlap, especially at room temperature, was large. The values obtained were 501 + 52 cal mol^{-1} (2.10 + 0.22 KJ mol⁻¹) and 521 + 24 cal mol⁻¹ $(2.18 \pm 0.10 \text{ KJ mol}^{-1})$. No measurements were possible in the vapour state because of the large overlap of the bands. Ethyl trans-Crotonate Investigations at different temperatures revealed that the equivalent lower pair of bands was very closely overlapped and was observed as a single asymmetrical band at room temperature at 1 184 cm⁻¹. At lower temperature. a lower shoulder was observed at 1 175 cm⁻¹. The higher wavenumber pairs of bands were again temperature dependent. The pair of bands at 1 275 and 1 264 cm⁻¹ were too closely overlapped to give an accurate ΔH^0 value, but they showed temperature dependence of a similar nature to the 1 307 and 1 294 cm⁻¹ bands which gave a $\triangle H^{\circ}$ value of 515 + 70 cal mol⁻¹ (2.16 ± 0.29 KJ mol⁻¹) using peak height measurements. Methyl Acrylate and Ethyl Acrylate Methyl acrylate and ethyl acrylate revealed two and one pairs of temperature dependent bands respectively in solution in carbon disulphide (-110° to 40°). The common pair of bands (at 1 290 and 1 276 cm⁻¹ in methyl acrylate and 1 296 and 1 271 cm⁻¹ in ethyl acrylate) were somewhat unsuitable for accurate variable temperature studies because of the presence of a small shoulder at 1 305 cm⁻¹ in both cases. The lower pair of bands in methyl acrylate at 1 202 and 1 180 cm⁻¹ gave a $\triangle H^0$ value of 315 ± 45 cal mol⁻¹



 $(1.32 \pm 0.19 \text{ KJ mol}^{-1})$. In ethyl acrylate a single broad band was observed at 1 194 cm⁻¹. The spectrum of methyl acrylate at room temperature and low temperature in the region 1 150 - 1 350 cm⁻¹ in solution is illustrated in Figure 12.

In both acrylates, the presence of 4 bands in the $950 - 1\ 000\ \text{cm}^{-1}$ region having C contours in the vapour has been mentioned (Figure 6). Using the peak height of the central Q branches, an approximate ΔH^0 value was calculated as $4^{\circ}0 \pm 100\ \text{cal mol}^{-1}\ (1.70 \pm 0.42\ \text{KJ mol}^{-1})$ based on measurements on the 968 and 963 cm⁻¹ bands in methyl acrylate at two temperatures 20° and 150° .

On the basis of comparison with $\sqrt{\beta}$ -unsaturated ketones, it was thought that the <u>s-trans</u> conformers of the $\sqrt{\beta}$ -unsaturated esters were more stable. Thus, since in all cases the high wavenumber band of each pair of bands increased in intensity on cooling, these high wavenumber components were thought to be associated with the <u>s-trans</u> conformer and the low wavenumber components with the <u>s-cis</u> or non-trans conformer.

4. Saturated Esters

The existence of a pair of bands in methyl esters of straight chain acids at about $1 \ 200 \ cm^{-1}$, (ethyl esters revealed a single band, sometimes with a low wavenumber shoulder) was similar to the observed situation in the methyl esters of acrylic and <u>trans</u>-crotonic acids which have been investigated. Variable temperature studies were, therefore, carried out on the methyl and ethyl esters of formic, acetic, propionic and n-butyric acids to establish whether a similar equilibrium occurred in saturated esters.

 ΔH° values where appropriate Methyl Propionate and n-Butyrate are shown in Table 9. The only clearly temperature dependent pair of bands occurred in methyl n-butyrate at 1 175 and 1 199 cm⁻¹. The variable temperature change in methyl n-butyrate is shown in Figure 13. AH^{O} values were calculated as 182 ± 60 cal mol⁻¹ (762 ± 251 J mol⁻¹) from peak height measurements and 115 ± 35 cal mol⁻¹ (481 \pm 147 J mol⁻¹) from peak area measurements in the temperature range -110° to 40° in carbon disulphide solution. A similar pair of bands was observed in methyl propionate and a slight variation with temperature was found equivalent to an enthalpy difference of 78 \pm 50 cal mol⁻¹ (327 \pm 209 J mol⁻¹). This figure itself might not have any significance, but taken in conjunction with the temperature variation of bands in methyl n-butyrate, it suggests a similar equilibrium might be possible in all saturated straight chain esters. The existence of evidence for conformational equilibrium in propionates and n-butyrates and the lack of evidence in formates and acetates 34,35,36 suggests that the conformers might be as shown.

70





	Antisym. C-C-O st. (cm ⁻¹)	∧H ^o cal. mol ⁻¹ from peak height measurements
Methyl formate	1206	
Methyl acetate	1241	an Arright an Arriense. An an Arriense Statestation an sa
Methyl propionate	1199 1175	78 <u>+</u> 50
Methyl n-butyrate	1195 1175	182 ± 60
Ethyl formate	1186	
Ethyl acetate	1242	-
Ethyl propionate	1186 (1167)	
Ethyl n-butyrate	1182 (1167)	
(Solution in CS2	-110° to +40°)	

TABLE 9 Conformations of esters of normal acids

These are similar to those found to exist in propionaldehyde⁴¹ where the cis form is found to be more stable. From this comparison, it is likely that the cis form is more stable in the saturated esters. There is no reason why this equilibrium should not exist in ethyl esters but in these, the bands which show evidence for this equilibrium are much closer together and variable temperature studies are not possible. A further equilibrium is also possible in the ethyl esters, as has been noted for ethyl formate³⁸, and this may make it more difficult to detect either equilibrium.

There is a similarity between the conformational equilibrium in certain saturated esters (propionates and n-butyrates) and certain $\mathcal{A}\beta$ -unsaturated esters (acrylates and <u>trans</u>crotonates), since both equilibria involve rotation of the $\mathcal{A}\beta$ C-C bond.



The mode of vibration which has been studied in both types of esters is thought to be similar, and is assigned to an antisymmetric C-C-O stretching vibration⁵⁴.



5. Other AB -unsaturated Esters

Speculative studies of methyl and ethyl 3.3.dimethylacrylates, methyl and ethyl methacrylates revealed no changes in their spectra with temperature suggesting either that they exist in virtually all one conformer of the enthalpy difference between the two conformers is very small. <u>Calculation of ΔS° Attempts to determine ΔS° were</u> unsuccessful. Straight line plots were not observed by the method of Fateley⁴⁴. The third band method of Mizushima⁴³ involved large errors in the $\triangle S^{\circ}$ values obtained and the assumptions made in this method were not felt to be justified. Errors The errors quoted in values of ΔH^0 were the standard deviation values calculated by statistical methods (Appendix No. 2). The standard deviation value quoted was a measure of the random error inherent in this method. In addition there may be significant systematic errors. Thus, in ethyl trans-crotonate using the pair of bands at 1 275 and 1 264 cm⁻¹, which were badly overlapped a value of $729 \pm 82 \text{ csl mol}^{-1}$ (3.05 + 0.34 KJ mol⁻¹) was calculated which was clearly well in excess of the 516 ± 71 cal mol⁻¹ (2.16 \pm 0.30 KJ mol⁻¹) obtained from the less badly overlapped pair of bands at 1 307 and 1 294 cm⁻¹. From

these figures, it was clear that values obtained from closely overlapped bands might well have serious errors.

Variation of $\triangle H^{\circ}$ with temperature would be indicated by curved plots of $\ln(A_1/A_2)$ against 1/T. Systematic deviations were not observed. However, in most cases, higher values of $\triangle H^{\circ}$ were obtained in the vapour over the temperature range 20° to 200° than in solution in the temperature range -110° to 40° . This may indicate that $\triangle H^{\circ}$ was temperature dependent or that the $\triangle H^{\circ}$ was intrinsically higher in the vapour state than in the carbon disulphide solution.

C ASSIGNMENT OF BANDS

The wavenumber values of vibrational bands of all the molecules studied in detail are listed in Table 10 and 11. The spectra in solution are shown in Figures (14 to 21). It is usual to assign fundamental modes of vibration of a molecule to certain localised movements of that molecule. This is not strictly valid since it involves the assumption that fundamental modes of vibrations are specific to changes in particular bond length, and particular angles and these changes are independent of the rest of the molecule. The degree of independence of a group vibration on the rest of the molecule can be assessed by carrying out a normal coordinate analysis of a particular molecule. For instance, calculations have been carried out on N-methylacetamide⁵⁵ revealing large coupling in the amide bands. Normal coordinate analysis is very complex for relatively small molecules and becomes progressively more difficult as the molecules increase in size particularly if they possess few elements of symmetry. It is found empirically

TABLE 10

Vibrational wavenumber values (cm⁻¹) of Acraldehyde, <u>Trans-</u>Crotonaldehyde, Methyl vinyl ketone and Ethylideneacetone

- 76 -

<u>Acraldehyde</u> CCl₄ solution : 3382w, 3100w, 3062w, 2998w, 2840m, 2805s, 2759s, 2700m, 2070w, 1926w, 1826w, 1703vs, 1615w, 1420m, 1403w, 1360s, 1274w, 1158s, 990s, 968s, 914s, 730w, 630w, 600w, 571w;

Vapour (band centres) 3428A, 3105A/B, 3070, 3004A/B, 2809B, 2759B, 2700B, 2060, 1918, 1824A/B, 1724A, 1625A, 1420A, 1361A/B, 1275A/B, 1160A, 993C, 959C, 915A/B, 798, 735, 593C, 569A;

<u>Trans-Crotonaldehyde</u> CCl₄ solution : 3374w, 3336vw, 3080wsh, 3042w, 3002w, 2982w, 2944w, 2916w, 2873vw, 2850wsh, 2808m, 2727m, 2696wsh, 2640vw, 2320w, 2152w, 1693vs, 1660wsh, 1641s, 1628m, (1540vw), 1444s, 1389m, 1375m, 1305w, 1253w, 1220w, 1146s, 1075s, 1042w, 1005m, 966s, 931s, (727vw), (665vw), 542m, 459vw;

Vapour (bard centres) 3420A/B, 3370, 3058, 3018, 2995, 2980, 2963, 2938A/B, 2880, 2811A/B, 2725A/B, 2175, 1720A, 1680sh, 1649A, 1455A/B, 1391, 1304A/B, 1147A, 1074A/B, 973C, 928C?, 730A, 544A/B, 464A/B;

<u>Methyl vinyl ketone</u> CCl₄ solution : 3360w, 3105w, 3065vw, 3025w, 3015w, 2980wsh, 2930w, 2850wsh, 1911w, 1707vs, 1687vs, 1648wsh, 1618m, 1425msh, 1401s, 1364s, 1295wsh, 1282w, 1250s, 1220wsh, 1181s, 1066w, 1055w, 1022msh, 997m, 987m, 960sh, 958s, 948msh, (824vw), (773w), (758w), 690w, 670wsh, 605w, 535vw, 492w, 427w;

Vapour (band centres) 3400, 3108A/B, 3030, 2977A/B, 2925, 2850, 1900, 1711, 1700, 1624A/B, 1440, 1402A/B, 1368, 1249A, 1180A, 1055, 1022, 1002C, 990C, 970, 953C, 800, 765, 692, 670, 610, 492;

Ethylideneacetone CCl₄ solution : 3395vw, 3340w, 3318w, 3036m, 3003w, 2973m, 2941m, 2920m, 2878w, 2858w, 1692s, 1674vs, 1645msh, 1632s, 1618msh, 1443m, 1438msh, 1427msh, 1379m, 1359s, 1314m, 1304wsh, 1292m, 1274m, 1252s, 1179m, 1166msh, 1105vw, 1065vw, 1042w, 1020w, 992msh, 974s, 948m, 938msh, 861w, (821vw), (801w), 622w, 608m, 565wsh, 548m, 502vw;

Vapour (band centres) 3385, 3045, 3020, 2970, 2955, 2935, 2870, 1700, 1640, 1618, 1445, 1438, 1365, 1316, 1294A/B, 1252A, 1177A, 1100, 1020, 974C, 940, 865, 820, 800, 605, 550;

s = strong; m = medium; w = weak; v = very; sh = shoulder. Values in brackets for thin films. TABLE 11 Vibrational wavenumber values (cm⁻¹) of methyl acrylate, methyl <u>trans</u>-orotonate, ethyl acrylate and ethyl <u>trans</u>-orotonate.

<u>Methyl acrylate</u> - <u>i.r.-CCl₄ solution</u> - 3448w, 3104w, 3070w, 3036wsh, 3024w, 2994m, 2951s, 2904w, 2890wsh, 2852w, 2832w, 2058w, 2035w, 1935w, 1729vs, 1633m, 1620msh, 1460wsh, 1438s, 1401s, 1360w, 1305wsh, 1290msh, 1276s, 1202s, 1180s, 1075s, 1002sh, 988s, 968s, 858m, (811m), 564m, 628w, 530vw, 470vw, 349w.

<u>Raman-liquid</u> - 3109w, 3062wsh, 3038m, 2994w, 2956m, 2856vw, 2838vw, 1729s, 1638vs, 1447w, 1406s, 1285m, 1212w, 1188w, 1076w, 1006sh, 976w, 864s, 821w, 671vw, 629w, 526w, 474m, 362w, 244m, 206w.

<u>I.r. - vapour</u> - 3440w, 3102w, 3030sh, 3002m, 2960m, 2920r, 2850v., 2045w, 1929w, 1749vs, 1633m, 1442s, 1406s, 1280m, 1205s, . . 1080m, 1005sh, 992m, 987m, 968m, 963m, 850sh, 814m, 660w. <u>Methyl trans-crotonate</u> - <u>i.r.-CCl₄ solution</u> - 3440w, 5062w, 3031w, 3000msh, 2980msh, 2958s, 2925m, 2860m, 1728vs, 1682w, 1663s, 1655sh, 1628w, 1508w, 1460sh, 1448s, 1438s, 1380m, 1335msh, 1315m, 1294m, 1275m, 1268m, 1196s, 1178s, 1109m, 1045m, 1030m, 1010sh, 973s, 940m, 908w, (842m), (730w), 692m, 630vw, 494w, 452m, 385w, 325m.

Raman-liquid - 3032v, 2953m, 2918s, 2851w, 1726s, 1662vs, 1453s, 1435w, 1383m, 1330wsh, 1307m, 1291wsh, 1200w, 1118vw, 1061w, 1039wsh, 945w, 915m, 861m, 735w, 706vw, 506w, 468w, 394vs, 333vw, 294vw.

<u>I.r. - vapour</u> - 3062sh, 3030sh, 2965m, 2935m, 2860w, 1748s, 1620m, 1445m, 1320m, 1275m, 1205sh, 1190s, 1105m, 1037m, 972m, 940sh, 910wsh, 840w, 730wsh, 690w, 450w. TABLE 11 (continued)

Ethyl acrylate - <u>i.r.-CCl₄ solution</u> - 3437w, 3105w, 3075vw, 3041wsh, 2995sh, 2984s, 2940msh, 2904msh, 2877wsh, 2049w, 1930w, 1724vs, 1638m, 1620m, 1478w, 1465m, 1447m, 1408s, 1388m, 1365w, 1305wsh, 1296s, 1271s, 1194vs, 1170sh, 1113wsh, 1096w, 1062m, 1030m, 988s, 967s, 917w, 899w, 859m, (808m), (769vw), 670w, 660w, 625vw, 530vw, 475vw, 385vw, 370w, 345w, 310w.

Raman-liquid - 3109ww, 3075vw, 3042m, 2971w, 2940s, 2903m, 2879w, 1724s, 1638s, 1623w, 1454m, 1411w, 1364vw, 1299m, 1285m, 1196w, 1116m, 1101vw, 1067w, 1032vw, 976vw, 906vw, 860s, 816vw, 792w, 614w, 474w, 374s, 316w, 254vw. <u>I.r. - vapour</u> - 3110w, 3050w, 2995m, 2960sh, 2900sh, 1930w, 1745s, 1635m, 1460w, 1410m, 1300m, 1275m, 1195s, 1100sh, 1070m, 1038m, 993m, 988m, 963m, 963m, 900w, 860w, 815m, 660w. Ethyl trans-crotonate - i.r.-CCl, solution - 3435w, 3058w, 3030w, 2984s, 2964sh, 2944s, 2920m, 2912sh, 2878w, 2858w, 1723vs, 1682sh, 1665s, 1655sh, 1525vw, 1479w, 1467w, 1445m, 1438m, 1391w, 1379m, 1368m, 1330w, 1307m, 1294m, 1275m, 1264m, 1184s, 1174sh, 1105m, 1048m, 1030m, 972m, 918w, 843m, (815w), (790w), (745w), (720w), 692m, 630vw, 500w, 399w, 356w, 327w, Raman-liquid - 3038w, 2982wsh, 2940sh, 2923m, 2879w, 2859w, 1720s, 1663vs, 1449s, 1380m, 1296s, 1270m, 1190m, 1117m, 1104m, 1048m, 972vw, 918w, 866m, 843sh, 719w, 692w, 510w, 400w, 362s.

<u>I.r. - vapour</u> - 3470w, 3070w, 2990m, 2960w, 2940w, 2880sh, 1745s, 1670m, 1455m, 1375m, 1310m, 1272m, 1189s, 1106m, 1052m, 976m, 920w, 850w, 690w.

s = strong; m = medium; w = weak; v = very; sh = shoulder. Values in parenthesis for thin films. that 'considerable coupling' can occur between stretching vibrations if the bonds have a common atom, between angle deformation and bond stretching if the bond is adjacent to the angle, and between angle deformations if they have a common bond⁵⁶. (Coupling is really a bogus concept used to consider in simple terms fundamental modes of vibration which involve more than one 'stretch' or 'bend'). As long as it is realised that an assignment to the vibration of a particular group infers that the fundamental mode of vibration is concerned mainly, but certainly not entirely, with the vibration of that particular group, these assignments are useful in discussing the structure of the molecule. The assignments have been made in terms of particular groupings present in one or more of these compounds.

The molecules studied have, at most, only a plane of symmetry in which case they belong to the C_g point group. Molecules with C_g symmetry containing N atoms have 2N-3 in-plane fundamental vibrations (A' class) and N-3 out-of-plane fundamental vibrations (A' class). Within each class there is no symmetry restriction to prevent mixing of vibrations involving different groupings. Some of the assignments of these molecules have been discussed previously. The infrared (vapour and carbon tetrachloride solution) and Raman (ethanol solution) spectra of acraldehyde have been assigned by Inuzuka⁵⁷. Harris⁵⁸ has also assigned the vapour spectrum recorded as far as 100 cm⁻¹. These assignments are generally similar except that Inuzuka assigned a band at 1 152 cm⁻¹ to a CH₂ rocking mode and a band at 1 270 cm⁻¹

TABLE 12.

Comparison of assignments of acraldehyde, <u>trans-crotonaldehyde</u>, methyl vinyl ketone and ethylideneacetone (cm.-1)

Mode				_M=M
$C = R_2 $ st R_2	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2808 (2727 (2x1389 = 2778	1055	1042
C = 0 st i.p. $C - R_2 \text{ def.}$ o.p. $C - R_2 \text{ def.}$	1703 1360 980	1693 1389 931	1687 1707 824 773	1674 1692 861
H C = C H C = C $Sym CH_2 st$ C - H st C = C st $sym CH_2 def.$ C - H rock C - H rock	3100 2998 3062 1615 1420 1274 914		3105 3025 3065 1648 1618 1401 1282 968	
o.p. CH = CH def.	990		997 987	

1 80

					a a construction of the second s	
	torsion	157				× · · · ·
	i.p. $CH(R) = CH - def$.		459	492		• • •
C' à la company	i.p. C - OR ₂ def.	571	(542)	690	622	2
o-c	skeletal C - C st	1158	1146	1250 1181	1252	117
ЯО					and a second	
	o.p. CMe H = CH def.		(542)?		548	8
	o.p. C - Me def.		784		80-	1
	o.p. CH = CH def.		966		97	4
	C - Me def.		727 665		60 62	8 2
ан 1997 - Пара Пара Пара (1997) 1997 - Пара Пара (1997)	sym CH def.		1305		131	4
	asym CH def.		1253		1274	129
	C = C st		1641		1645	163
	C - Me st		1075		(106)	5)
H	sym CH st		3002		300	3
C = C	asym CH st		3042		303	6
·	o.p. $CH = CH_2$ def.	600		605?		
	o.p. CH ₂ def.	968		958		

• 18

¢ È

			1	T	1
	CTI		(2873		2878
3 - 0 = 0	syn CH st		(2850		(2858)
	i.p. asym CH ₃ st		(2982 (2944 (2916		((2973) (2920 ((2941)
•	sym CH ₃ def.		1375		1379
	i.p. asym CH ₃ def.				1443
	o.p. asym CH, def.				(1438)
	i.p. CH ₃ rock		1109		1105
	o.p. CH rock		1042		1020
	CH ₃ torsion				
$_{3} - C = 0$	sym CH ₃ st			2850	(2858)
	i.p. asym CH ₃ st			(2980	(2973)
•	o.p. asym CH ₃ st	• • • •		(2930	((2941)
	sym CH ₃ def.			1364	1359
	i.p. asym CH ₃ def.			£ 1425	(1438)
	o.p. asym CH ₃ def.				1427
	i.p. CH ₃ rock			1066	(1065)
	o.p. CH_ rock			1022	992
			1 · · · · · · · · · · · · · · · · · · ·		

Bands in parenthesis assigned twice

of vibration

.

82 2 1

1

1 270 cm⁻¹ to a vinyl C-H bending motion on the basis of comparison with the clearly related molecules glyoxal and butadiene. The C=O and C=C stretching vibrations of methyl vinyl ketone and ethylideneacetone have been assigned¹⁹. An assignment of methyl acrylate has been attempted at the same time as its structural isomer, vinyl acetate⁵⁹. A partial assignment of methyl and ethyl acrylate and methyl trans-orotonate has been attempted⁶⁰. The assignments are shown in Table512 and 13.

C=O and C=C Stretching Modes

The carbonyl and ethylenic double bond stretching vibrations are common to all the molecules studied. Single bands are observed for the carbonyl vibration at 1 703 cm⁻¹ and 1 693 cm⁻¹ in acraldehyde and <u>trans</u>-crotonaldehyde with the expected A contour for the vapour state. The two carbonyl bands of methyl vinyl ketone and ethylideneacetone, corresponding to the two conformers have already been noted¹⁹. In the

 \checkmark -unsaturated esters where two carbonyl bands would again be expected corresponding to the two conformers, only one asymmetrical band is observed close to 1 725 cm⁻¹. This can be rationalised at least empirically by reference to certain furan derivatives¹⁶. Both 2-furancates and 2-keto furans have been thought to show evidence for both <u>s-trans</u> and <u>s-cis</u> conformers. The separation in wavenumbers of the <u>s-cis</u> and <u>s-trans</u> carbonyl bands of a carbonyl group conjugated to an olefinic double bond in the furan derivatives reduces from 28 cm⁻¹ in the ketone to 12 cm⁻¹ in the ester. If a similar

-unsaturated ester	S	
Məthyl acrylatə	Ethyl aorylate	Methyl <u>trans</u> crotonate

Ethy1 trans crotonate

TABLE 13 Assignments of fundamental modes of vibrations in

H H H C

Mode

asyn CH ₂ st	3104	3105
syr CH ₂ st	2994	2995
C-H st	3036	3041
C=C st	1633 (1620)	1638 (1620)
i.p. sym CH def	1401	1408
i.p. C-H rock	1290 1276	1296 1271
i.p. CH ₂ rock	950	917
o.p. CH=CH def	988 (992 987) vapour	988 (993 988) vapour
o.p. CH ₂ def	968 (968 96 3)	967 (968 963)
	vaporr	vapour
o.p. CH=CH, def	664	660

CH. H H ٤

asym CH st			3062		3058	
syn CH st			3031		3030	
C-Me st			1045		1048	
C=C st			1663(1682	2,1655)	1665(16	582,1655)
i.p. asym CH def		•	1275	1268	1275	1264
syn CH def	• # •		1315	1294	1307	1294
i.p. C-Me def			692		692	
o.p. CH=CH def			97 3		972	
o.p. C-Me def			730		720	
o.p. CHMe≡CH def			494		500	

TABLE 13 (continued)

Mode	Methyl acrylate	Ethyl acrylate	Methyl <u>trans</u> crotonate	Ethyl <u>trans</u> crotonate
^{CH} ℑ _{C=C}	21			
sym CH_ st			2860	2858
i.p. asym st			3000 (2980)	2984
o.p. asym st	· · ·		2925	2920
sym CH, def			1335	1330
i.p. asym CH, def			1448	1445
o.p. asym CH, def			1438	1438
i.p. CH _z rock			1109	1105
o.p. CH _z rock		•	1030	1030
CH ₃ torsion			?	?
C=O st	1729	1724	1728	1724
R-C and CO sym st	858	859	842	843
R-C and CO asym st	1202 1180	1194	1196 1178	1184 (1174)
R ¹ -0 st	1075	1062	1109	1105
C≷0 i.p. bend	629	625	630	630
C-C=O i.p. bend	349	• • •	325	• • • • • • • •
C-O-C i.p. bend	470	475	385	356
C-O-C o.p. bend	244	•••	× × • • •	• • •
i.p. Skeletal def	530	• ••	452	•••
o.p. Skeletal def	- 206	- · · • • •	294	•••
o.p. Skeletal def	114	160	•••	

N.B. the last seven assignments in this group are very problematic.

TABLE 13 (continued)

Mode	Methyl acrylate	Ethyl acrylate	Methyl <u>trans</u> crotonate	Ethyl <u>trans</u> crotonate
			ан ай 1 ал ан	
CCH 3	· · · ·	, .		
sym CH ₃ st	2852		2858	
i.p. asym CH _z st	2951		2951	
o.p. asym CH _z st	2904		2925	
sym CH ₃ def	1360	<i>*</i> *	1380	
i.p. asym CH ₃ def	1460		1460	
o.p. asym CH ₃ def	1438		1448	
i.p. CH ₃ rock	1002		1010	
o.p. CH _z rock	ka ● ● ● ● ●		940	
CH ₃ torsion	114		?	•
and a second second Second second				
O-CH2-CH3	r			
sym CH ₂ st		2877		2878
asym CH ₂ st		2904	· · · · · · · · · · · · · · · · · · ·	2912
i.p. CH ₂ bend		1478		1479
o.p. CH2 bend	••	1388		1391
i.p. CH ₂ rock	N	1096		?
ethyl torsion		?		? • • •
o.p. CH ₂ rock		1030		?
i.p. C-C st		1113		1105
o.p. O-C-R bend		769	· · · ·	745

TABLE 13 (continued)

Mode	Methyl acrylate	Ethyl acrylate	Methyl <u>trans</u> crotonate	Ethyl <u>trans</u> crotonate
			· · · ·	
R-CH	·	<i>,</i>		
syn CH ₃ st		2877		2878
i.p. asvm CH ₃ st		2984		2984
o.p. asym CH ₃ st		2940		2944
sym CH ₃ dof		1365		13 68
i.p. asym CH ₃ def		1465		1467
o.p. asym CH def		1447		1445
1.p. Ch. rock		1096		• • • •
0.p. CH ₃ rock		1030		••••
CH3 torsion	•	1030		••••
				•

 Total no. of vibration
 21 i.p. + 9 o.p. 27 i.p.+12o.p. 27i.p.+12o.p. 33i.p.+15o.p.

 39
 = 39

 = 30
 39

reduction of 16 cm⁻¹ occurs between the acyclic -4β -unsaturated ketones and the acyclic -4β -unsaturated ester; the separation of the two conformers would drop to 3 cm⁻¹ (Table 14). It would not be possible to distinguish two bands with this separation unless they were unusually sharp. (The same rationale would predict that the separation in acyclic -4β -unsaturated aldehydes would be 15 cm⁻¹ which should be easily observed).

The C=C stretching vibration in these molecules would be expected to be a useful band for detecting the presence of conformers. This has been found to be the case in ethylideneacetone where two C=C vibrations are observed. However, in methyl vinyl ketone, the C=C stretching vibration for the two conformers are presumed to occur at the same wavenumber value since only one band is observed. In the

 $d\beta$ -unsaturated esters where splitting occurs it is not possible to detect any temperature dependence which could relate this splitting to conformational equilibrium. The splitting is considered⁷¹ to be caused by Fermi resonance. A possible component for such a resonance in methyl and ethyl acrylates is the overtones of the bands near 810 cm⁻¹. In acrylates two components are observed at 1 635 and 1 620 cm⁻¹. In <u>trans</u>-crotonates, there are both high and low wavenumber components of the main band. The high wavenumber component at 1 682 cm⁻¹ is probably due to resonance involving the overtones of bands near 840 cm⁻¹. The low wavenumber components may be caused by rotational isomerism but this band is not sufficiently resolved to be studied successfully by variable temperature effects. It is of interest that a strong Raman

- 88 -



TABLE 14 Comparison with furan derivatives

band occurs at the same wavenumber as the main infrared spectra of the acrylates and <u>trans</u>-crotonates. The Raman bands are at 1 638 cm⁻¹ in the acrylates and near 1 664 cm⁻¹ in the <u>trans</u>-crotonates (see Table 11). These observations confirm the assignments of these wavenumber values to the C=C stretching motions. The general absence of additional components in the Raman (a weak extra band is observed at 1 623 cm⁻¹ only in ethyl acrylate), suggest that the additional infrared components to the C=C stretching vibration are the result of Fermi resonance (evidently weak in the Raman) rather than the result of conformational equilibrium (expected to lead to strong bands in the Raman).

Aldehydic C-H Modes

The assignments of the fundamental modes associated with the aldehydic group should be closely similar in acraldehyde and <u>trans</u>-crotonaldehyde. It has been noted that an aldehydic C-H stretching mode was split into two bends because of Fermi resonance interaction with the overtone of the C-H bending vibration.⁶¹ In <u>trans</u>-crotonaldehyde, two bands are observed at 2 727 and 2 808 cm⁻¹ in solution with AB hybrid contours in the vapour state. The C-H bending vibration is assigned at 1 389 cm⁻¹, and will have an overtone at about 2 780 cm⁻¹. In aoraldohyde, four bands are observed in solution at 2 700, 2 759, 2 805, and 2 840 cm⁻¹ the first three being evident in the vapour with B contours. It is clear that more than one interaction is present and various overtones, listed in Table 12 are thought to contribute to the Fermi resonance interaction with the C-H aldehydic stretch.





The contours and fine structure of these bands suggest that the dipole change associated with the aldehydic C-H stretching mode is virtually parallel to the B axis in acraldehyde. The out-of-plane aldehyde C-H bending motion has been calculated at 980 cm⁻¹ in acraldehyde from studies of the deuteriated compound⁶². It would therefore be overlapped by the band at 990 cm⁻¹. This suggests that the band at 931 cm⁻¹ in trans-crotonaldehyde may be the C-H out-of-plane bending mode although the contour of this band is masked by the proximity of the band at 966 cm⁻¹.

Ketonic C-Me Modes

The C=O vibration has already been discussed separately. The C-Me stretching and bending modes are likely to interact with other modes, but the appearance of weak bands at 1 055 and 1 042 cm⁻¹ in methyl vinyl ketone and ethylideneacetone respectively lead to their assignment as C-Me stretches and the appearance of bands in the region 770 - 860 cm⁻¹ without counterparts in acraldehyde and <u>trans</u>-crotonaldehyde suggests assignment to the C-Me out-of-plane deformation. It is not possible to observe contours of any of these bands in the vapour state.

Skeletal Modes of =C-C= Grouping

In the aldehyde and ketone molecules, four skeletal modes might have been expected. The most prominent of these involved considerable =C-C- stretching although it is probably coupled with the adjacent C-R in the ketones. It occurs at about 150 cm^{-1} in the aldehydes with an A contour. In the ketone, it occurs as two bands at about 1250 cm^{-1} (s-trans) and





1 180 cm⁻¹ (<u>s-cis</u>) which are the most suitable pair for conformational equilibrium studies in the ketones. The other skeletal modes are less clearly defined although the torsion has been observed in acraldehyde⁵⁸.

Ester Grouping Modes

The fundamental modes associated with the ester grouping apart from the carbonyl vibration are somewhat difficult to assign, because of the complexity of the group. The strong band which usually occurs in esters at 1 200 cm⁻¹ has been usually assigned as a C-O vibration. It is thought to be more correctly described as an antisymmetrically coupled vibration involving mainly C-C(carbonyl) and C(carbonyl)-O vibrations. A similar assignment has been suggested in methyl acetate²⁴. This band appears to be split for the s-trans and s-cis molecules in the methyl esters of acrylic and crotonic acid and this pair of bands is temperature sensitive. The bands appear at 1 196 and 1 178 cm⁻¹ for methyl crotonate and 1 202 and 1 180 cm⁻¹ for methyl acrylate. In the ethyl esters, separate bands are less clearly visible. A deuteriation study⁶³ showed that the pair of bands in methyl crotonate appeared to move to higher wavelength at 1 260 and 1 244 cm⁻¹. This suggests that no hydrogen bending is involved, and the change to higher wavenumber is the result of a slight change in the nature of the vibration.

Bands at approximately 1 070 cm⁻¹ in acrylates and 1 100 cm⁻¹ in crotonates are assigned to the aliphatic C-0 stretch. Attempts to assign other vibrations to bending and skeletal vibrations are somewhat problematic but approximate assignments are attempted

- 56 -





99 εA. 100 * 2000 Figure 19 a) Infrared Spectrum of ethyl acylate (4000 - 1700 cm⁻¹) ଟ CH-3000 , ir 4000 - (%) SHAAT 4


in Table 13.

Vinyl Modes

The only differences between the assignments of the present work and that of Harris⁵⁸ for acraldehyde occur in the assignment of the vinyl C-H stretching modes. Only two bands are clearly observed in the appropriate region of the vapour spectrum at 3 004 cm⁻¹ and 3 105 cm⁻¹. However, comparison with solution spectra indicates the presence of a third band at 3 062 cm⁻¹. This band which was not observed by Inuzuka⁵⁷ is assigned to the olefin C-H stretching mode associated with the single hydrogen. Its vapour contour is masked by the bands at 3 004 and 3 105 cm⁻¹ which have A/B hybrid contours and which are assigned to the symmetric and anti-symmetric CH₂ stretching modes respectively. These assignments are in accord with assignments of vinyl modes in acrylates⁵⁹. Similar assignments are suggested for methyl vinyl ketone.

The out-of-plane vinyl bands of acraldehyde, methyl vinyl ketone, and acrylate esters are sensitive to environment. In methyl vinyl ketone, the vibration due to the out-of-plane -CH=CH deformation (twist) is split into two bands for the <u>s-trans (997 cm⁻¹)</u> and <u>s-cis (987 cm⁻¹)</u> conformers. In the vapour of methyl and ethyl acrylate both the twist and the wag (out-of-plane CH deformation) are split for the two conformers (992 and 968 cm⁻¹ for <u>s-trans</u> and 987 and 963 cm⁻¹ for <u>s-cis</u> in methyl acrylate and virtually the same values for ethyl acrylate). The calculated spacings of the three out-of-plane vinyl modes are less than 0.5 cm⁻¹ in both methyl vinyl ketones and the acrylates (Table 2). This explains the absence of fine structure of these bands which is present in the corresponding bands in the acraldehyde. However, the prominent central Q contours have already been mentioned.

The in-plane bending and rocking vibrations of the vinyl group have been assigned. It is interesting to note that the C-H rocking vibration (assigned at about 1 280 cm⁻¹) appears to be different for the two conformers in the acrylates.

The approximate forms of vibration of the CH_z-CH=CHgrouping should be similar in crotonaldehyde, ethylideneacetone and esters of crotonic acid. The C-H stretching modes occur at the expected wavenumbers. The in-plane symmetric and antisymmetric C-H bending deformation modes appear to occur at different wavenumber values for the two conformers in the transcrotonates and were temperature dependent. The antisymmetric deformation also appears to occur at different wavenumber values for the two conformers in ethylideneacetone but not the symmetric in-plane mode. In both ethylideneacotone and trans-crotonates, support for the assignment of the higher wavenumber bands (E. 1314 cm^{-1} and M.C. 1315 and 1 294 cm^{-1}) to the symmetric mode and the lower bands (E. 1 292 and 1 274 cm⁻¹ and M.C. J 275 and 1 268 cm⁻¹) to the antisymmetric mode is shown in the Raman. The Raman bands of the higher pair are strong or medium in intensity, whereas the Raman bands of the lower pair are weak or absent. The out-of-plane deformations involving in phase hydrogen deformations is observed in all the ethylidene grouping compounds at about 960 cm⁻¹. In crotonaldehyde the band is observed with a

- 102 -









contour and fine structure is just observable (calculated and observed spacings are shown in Table 2 and 4). It is a little surprising that this vibration is not split in either ethylidenescetone or the <u>trans</u>-crotonates since the equivalent mode is split in methyl vinyl ketone and the acrylates. These results suggest that the position (in cm^{-1}) of the out-ofplane deformation of the trans C-H groups is less sensitive to conformational changes in a <u>trans</u>-substituted ethylene group than in a vinyl group. The out-of-plane mode involving CHMe=CH deformation is expected to be strong in the Raman spectrum. Bands at 784, 801 and 750 cm⁻¹ in <u>trans</u>-erotonaldehyde, ethylidenescetone and the <u>trans</u>-crotonate esters are nocordingly assigned to this mode. The other modes of the ethylidene group are tentatively assigned but the evidence is inconclusive. Methyl and Ethyl Modes

The assignments of the modes of the methyl groups are likely to be slightly different in molecules having an adjacent C=C, C=O, O-C or CH₂ groups however they should be very similar and in many cases the vibrations are assigned twice to the equivalent modes of different methyl groups. For instance, it is well known that for CH₃C=O, the C-H stretching vibrations and the C-H antisymmetric deformation are weak and the C-H symmetric deformation strong relative to the corresponding vibrations in CH₃C=C. Assignments of the three types are unequivical in methyl vinyl ketone, (CH₃C=O) <u>trans</u>-orotonaldehyde (CH₃C=C) and methyl acrylate (OCH₃). Slightly differing values are observed for the C-H stretching vibrations. The symmetric and antisymmetric deformations are 10 or 20 cm⁻¹ lower in the $CH_3C=0$ grouping to the $CH_3C=C$ grouping. The rocking vibrations are assigned to bands in the region 900 - 1 100 cm⁻¹. They occur at much lower wavenumbers in the OCH_3 group. It is well known that the so-called CH_3 rocking vibration is particularly sensitive to the atom to which it is attached.

The CH₂ group vibrations occur at the expected wavenumbers in the ethyl esters, but in most cases the methyl vibrations overlap and occur at similar wavenumbers.

It is interesting to note the vibrational modes which appear to be sensitive to the conformer present (Table 15). The C=O and C=C vibrations are sensitive in certain cases. Certain skeletal modes of vibration are also different in ketones and esters in the two conformers.



in ketones

e.g.

in esters

Some of the modes of the ethylenic double bonds can also show evidence of conformations. From the present studies it is thought that the vinyl out-of-plane modes, the wag and the twisting are particularly useful in the vapour state for showing evidence of the existence of the two conformers in vinyl systems. The C-H in-plane rocking vibration in vinyl systems also appears to be sensitive to conformation in acrylates. In the ethylidene

TABLE 15 Vibrational modes which can be used to detect conformational change.

Mode	Compound	Wavenumber value (cm ⁻¹)		
	· · · · · · · · · · · · · · · · · · ·	s-trans	8-018	
Skeletal C-C stretch	Methyl vinyl ketone	1250	1181	
	Ethylideneacetons	1252	1179	
Carbonyl	Methyl vinyl ketone	1687	1707	
stretch	Ethylideneacetone	1674	1692	
o.p. CH=CH def.	Methyl vinyl ketone	99 7	987	
,	Methyl acrylate (vapour only)	992	98 7	
	Ethyl acrylate (vapour only)	99 3	988	
o.p. CH ₂ def.	Methyl acrylate (vapour only)	968	96 3	
	Ethyl acrylate (vapour only)	968	963	
C=C stretch	Ethylideneacetone	1645	1632	
Antisymmetric	Methyl <u>trans</u> - crotonate	1196	1178	
	Methyl aorylate	1202	1180	

TABLE 15 (continued)

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Mode	Compound	Wavenumber valu (cm ⁻¹)		
		<u>s-trans</u>	<u>s-cis</u>	
Symmetric	Methyl <u>trans</u> -crotonate	1315	1294	
isp. CH def.	Ethyl <u>trans</u> -crotonate	1307	1294	
Antisymmetric	Ethylideneacetone	1274	1292	
Tebe ou dere	Methyl <u>trans</u> -crotonate	1275	1268	
	Ethyl <u>trans</u> -crotonate	1275	1264	
i.p. C-H rocking	Methyl acrylate	1290	1276	
me tang a Broups	Ethyl aurylate	1296	1271	

grouping, the out-of-plane vibrations appear to be less sensitive, but the in-plane symmetric and antisymmetric C-H deformation can show evidence of conformational change. All these vibrations might be expected to be sensitive to the <u>s-cis</u> - <u>s-trans</u> isomerism in related molecules.

CHAPTER IV

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

A Determination of Parameters in Three Spin Systems and Other Systems

B Temperature and Solvent Studies

The object of examining the proton N.M.R. spectra of these compounds is to assign the chemical shift (the shift in Hz between each proton and the protons of tetramethylsilane $(CH_{3})_{A}Si)$ and the coupling constant (J_{AB}) between any two protons H_A and H_B for which spin-spin coupling takes place. The N.M.R. parameters obtained can be considered in relation to possible conformational equilibrium of the compounds examined. The N.M.R. spectra of these systems involving either two trans ethylenic protons or three vinyl protons, present some difficulties in interpretation since these olefinic resonance cannot be related to the parameters & and J in a simple or 'first order' manner. These systems must in general be treated by 'second order' methods. The criteria for deciding which is the simplest method to apply to a particular spin system depends on the magnitude of the $\left(\begin{array}{c} \delta_{12}/J_{12} \end{array} \right)$ ratios where $\begin{array}{c} \delta_{12} \end{array}$ is the difference in chemical shift of two protons with a coupling constant between these protons given by J_{12} . Thus in a system with two protons strongly coupled (i.e. $(\delta/J)_{12}$ is small) known as an AB system, a different treatment is necessary to that employed for a weakly coupled pair of protons $(\delta/J)_{12}$ is large), known as an AX system. A detailed discussion of the three spin case is presented followed by a short account of the other complex systems which are present in these molecules.

- 113 -

- A DETERMINATION OF N.M.R. PARAMETERS IN A THREE SPIN SYSTEM AND OTHER SYSTEMS
- 1: Validity of Different Approaches to the Three Spin System

Since vinyl groupings are present in nome of the molocules studied in detail (methyl vinyl ketone and methyl acrylate) and the three spin system is relatively complex to interpret, a study of the most suitable methods applicable to various (\mathcal{S}/J) ratios was undertaken. In each case the protons can be labelled so that (\mathcal{S}/J)_{AB} \leqslant (\mathcal{S}/J)_{BC} \ll (\mathcal{S}/J)_{AC}. The simplest ireatment necessary to give correct values of coupling constants (errors \ll 0.1Hz) and chemical shifts (errors \ll 0.3Hz) is shown in Table 16.

TABLE 16 The conditions of validity of different treatments for a three spin system

Treatment	Conditions of Validity
AMX	$\frac{\sum_{AM}}{J_{AM}} > 23; \qquad \frac{\sum_{MX}}{J_{MX}} > 20;$
ABX	$c.5 < \frac{\hat{S}_{AB}}{J_{AB}} < 20; \qquad \frac{\hat{S}_{BX}}{J_{BX}} > 10;$
ABK	$0.5 < \underbrace{\int_{AB}}_{J_{AB}} < 1C; 3 < \underbrace{\int_{BK}}_{J_{BK}} < 10;$
ABC	$\frac{\delta_{AB}}{J_{AB}} < 3; \qquad \frac{\delta_{BC}}{J_{BC}} < 3;$

The methods indicated will be described in the next section. When the parameters are calculated based on different treatments, different errors occur which are dependent on the various C/Jvalues. These differences are illustrated by a series of hypothetical systems in Table 17. For this purpose the coupling constants have been taken as $J_{12} = 18Hz$, $J_{13} = 2.0Hz$, $J_{23} = 10Hz$ which would be appropriate for a vinyl system.



A graph has also been drawn to illustrate the hypothetical cases chosen (Figure 22).

Different parameters have also been obtained by the various treatments in the real spectra of methyl vinyl ketone. These are illustrated in Table 18 (a). In this case the (\sqrt{J}) ratios are as follows.

$$\left(\frac{\zeta}{J}\right)_{AB} = \frac{19.3}{17.8}; \qquad \left(\frac{\zeta}{J}\right)_{\mathcal{BC}} = \frac{43.7}{10.6}; \qquad \left(\frac{\zeta}{J}\right)_{\mathcal{AC}} = \frac{24.3}{1.1};$$

- 1.1;





Even more striking errors in the simpler approaches are shown for methyl acrylate (see Table 18(b)).



TABLE 17 Accuracy of Different Treatments on

Hypothetical Systems

Position	Treatment	Parameters (Hz) and Errors					
Graph O/J ratios		1	2	3	J ₁₂	J ₁₃	^J 23
1 ∂/J ₁₂ ≖20	True values Calculated AMX Errors	360.0 360.2 0.2	0.0 -0.1 -0.1	-200.0 -200.1 -0.1	18.0 18.0 0.0	2.0 2.0 0.0	10.0 10.0 0.0
2 δ/J ₁₂ =5 d/J ₂₃ =20	True values Calculated AMX Errors Calculated ABX Errors	90.0 90.9 0.9 90.0 0.0	0.0 -0.8 -0.8 0.1 0.1	-200.0 -200.1 -0.1 -200.1 +0.1	18.0 18.0 0.0 18.0 0.0	2.0 2.1 0.1 2.0 0.0	10.0 9.9. -0.1 10.0 0.0
3 4 J ₁₂ =2	True values Calculated AMX Errors Calculated AEX Errors	36.0 38.1 2.1 36.0 0.0	0.0 -2.0 -2.0 +0.1 0.1	-200.0 -200.1 -0.1 -0.1 -0.1	18.0 18.0 0.0 18.0 0.0	2.0 2.4 0.4 2.0 0.0	10.0 9.6 -0.4 10.0 0.0
4 $\sqrt[3]{J}_{12}=0.5$	True values Calculated AMX Errors Calculated ABX Errors	9.0 14.8 5.8 9.0 0.0	0.0 -5.6 -5.6 +0.2 +0.2	-200.0 -200.1 -0.1 -200.1 -0.1	18.0 18.0 0.0 18.0 0.0	2.0 4.2 2.2 1.9 -0.1	10.0 7.8 -2.2 10.1 +0.1
5 \$1 ₁₂ =4 \$12=10	True values Calculated AMX Errors Calculated ABX Errors	72.0 73.1 1.1 72.0 0.0	0.0 -0.8 -0.8 +0.3 +0.3	-100.0 -100.3. -0.3 -100.3 -0.3	18.0 18.0 0.0 18.0 0.0	2.0 2.1 +0.1 2.0 0.0	10.0 9.9 -0.1 10.0 0.0
6 5/J 12=2 5/J 23=4	True values Calculated AMX Errors Calculated ABX Errors	36.0 38.2 2.2 36.1 0.1	0.0 -1.5 -1.5 0.6 0.6	-40.0 -40.7 -0.7 -40.7 -0.7	18.0 17.8 -0.2 17.8 -0.2	2.0 2.6 +0.6 2.2 +0.2	10.0 9.6 -0.4 10.0 0.0
	Errors	0.0	0.0	-40.0 0.0	0•0 T0•0	2.0	0.0

TABLE 17 (continued)

Position	Trea	Treatment			Parameters (Hz) and Errors				
on Graph C/J rati	08		1	2	3	J ₁₂	^J 13	^J 23	
7 S/J 12 S/J 23	=1.0 True Calo Erro =2.0 Calo Erro Calo Erro Calo Erro	values ulated AMX rs ulated ABX rs ulated ABK rs ulated ABC rs	18.0 21.9 3.9 18.1 0.1 18.1 0.1 18.0 0.0	0.0 -2.4 -2.4 +1.4 +1.4 0.1 0.1 0.0 0.0	-20.0 -21.5 -1.5 -21.5 -1.5 -20.2 -0.2 -20.0 C.0	18.0 17.1 -0.9 17.1 -0.9 17.6 -0.4 18.0 0.0	2.0 4.0 2.0 2.9 0.9 2.4 0.4 2.0 0.0	10.0 9.0 1.0 10.0 0.0 10.0 0.0 10.0 0.0	

Values are chosen so that $\left(\left(\frac{\delta}{J}\right)_{12} \ll \left(\frac{\delta}{J}\right)_{23} \ll \left(\frac{\delta}{J}\right)_{13}\right)_{13}$ N.B.

118 -

Observed

Calculated by different methods

;

(313)	AMX	ABX	ABK	ADC	Intensities
10.0	-0.53	-0.74	0.01	0.00	0.76
K 2.65	2.91	2.13	2.63	2.65	0.77
$\binom{(c)}{(x)}$ 9.35	8.01	8,52	9•39	9.36	1.05
12.00	11.44	11.39	12.01	12.00	1.34
17.45	14.56	17.62	17.51	17.50	0.16
20.15	18.00	20.49	20.13	20.15	0.53
35.20	32.23	35.14	35.16	35.16	2.02
37.80	35.67	38.01	37.78	37.80	1,36
/41.05	44 •47	41.66	41.00	41.02	2.08
50.40	53.01	50.92	50.38	50 •3 8	1.23
В) (м) 58.65	62.15	59.17	58.65	58.67	0.31
68.00	70.69	68.44	68.03	58.03	0.31
32.85	37.92	32.56	32.88	32.07	?
Zero inten	sity for o	ther two p	possible l	ines	•
ν_{c}	6.0	6.0	6.73	6.72	
ک	54 •5	51.12	50.39	50.40	
\mathcal{V}_{Λ}	27.65	31.07	31.05	31.06	
\mathbf{J}_{BC}	9•35	10•49	10,68	10.66	
J _{AC}	2.65	1.51	1.12	1.15	
$\mathbf{J}_{\mathbf{AB}}$	17.65	17.65	17.85	17.85	

Units - Hz

TABLE 18(b) Acouracy of treatments illustrated for methyl acrylate

(Observed	(Calculated	by diffe	rent method	18
((335+)	AMX	ABX	ABK	ABC	Intensities
	0.0	-1.55	-1.68	-1.55	-0.01	0.28
(4.3	3.30	2.80	3.62	4.29	0.62
((K)9 .1	7.43	7.78	8.64	9.10	1.08
((X)13.4	12.28	12.27	13.81	13.41	1.52
	12.2	10.95	13.61	12.65	12.26	0.86
- 	21.4	19.93	23.08	22.84	21.39	0.05
•-	B 28.9	27.22	29.76	29.29	28,95	2.24
().	1) 38 . 1	36.20	39.23	39.48	38.07	1.34
	36.9	39•79	37.27	36.20	36.94	1.86
A	41.2	44.65	41.76	41.37	41.25	1.22
	53.6	56.06	53.42	52 . 83	53.62	0,28
	57•9	60,92	57.90	58.01	57.92	0.14
_0	845-083	-21.41	-15,88	-14.90	-15.56	0.01
No No	28.9	32.15	26.46	27.17	28.96	0.50
0		68 .5 7	68.72	67.04	65.90	0.01
V	ſc	6.7	6.7	8,2	8.8	
V	B	25.2	29.1	27.8	27.9	
v	A	47•4	43.5	43.2	42.6	
J	DC -	9.1	10.6	. 10.2	11.3	, ,
J	AC	4•3	2.8	2.5	0.3	
J	ΔB	16.7	16.7	17.4	18.5	

2. Actual Treatments of Three Spin Systems

a) <u>AMX</u> In an AMX spectrum, 12 lines are expected. The appropriate separations give the value of the coupling constants by direct measurement and the chemical shifts are given by the average of the four lines associated with each proton.



b) <u>ABX</u> In an ABX spectrum, the spectrum may consist of 14 lines (the two extra combination lines are usually weak in an ABX system). A similar treatment as that for an AMX system, leads to errors in the chemical shift and the coupling constants as derived by direct measurement of the spectrum. However, the basic 12 lines are usually clear and are assigned to obey the following subtraction and addition rules.

 $3-1=4-2=7-5=8-6=|J_{AB}|;$ 2-1=4-3=11-9=12-10; 10-9=12-11=6-5=8-7; $|(10-11)|=|(8-4)|\cdots|(5-1)|;$ $|J_{AX}+J_{BX}|=|12-9|;$ $2D_{+}=6-2=8-4;$ $2D_{+}=5-1=7-3;$

 $V_{A+B} = (1+2+3+4+5+6+7+8)/4 V_X = (3+10:11+12)/4;$ Thus D₊, D₋, |J_{AB}|, |J_{AX}+J_{BX}|, V_{A+B}, V_X can be obtained from the spectra

- 12! -

$$V_{A-B} + \frac{1}{2}(J_{AX} - J_{BX}) = (4D_{+}^2 - J_{AB}^2)^{\frac{1}{2}}$$
 (1)

$$v_{A-B} - \frac{1}{2}(J_{AX} - J_{BX}) = (4D_{-}^2 - J_{AB}^2)^{\frac{1}{2}}$$
 (2)

Thus by subtraction of (2) from (1), a value of $|J_{AX} - J_{BX}|$ can be obtained and by addition a value of V_{A-B} . Thus $|J_{AX}|, |J_{BX}|, V_A, V_B$ can be determined. c) <u>ABK⁶⁵</u> The ABK treatment assigns the lines in the same way as for an ABX system. Correction terms are then calculated dependent on the ABX calculated values of coupling constant and on the separation of certain lines.

 ϕ_{\perp} and ϕ_{\perp} can be calculated from D₁ and D₂.

 $\sin 2\phi_{+} = J_{AB}^{2D_{+}};$ $\sin 2\phi_{-} = J_{AB}^{2D_{-}};$

From these four correction terms are calculated

$$\begin{array}{rcl} & & & & & \\ & & & & \\ & & & & \\ & & & \\ &$$

Approximate values of Δ_{23} , Δ_{24} , Δ_{57} and Δ_{67} can be obtained from the spectra

$$\Delta_{24} = 8 - 12 = 7 - 11$$

$$\Delta_{23} = 4 - 12 = 3 - 10$$

$$\Delta_{67} = 1 - 9 = 2 - 11$$

$$\Delta_{57} = 5 - 9 = 6 - 10$$

The values of the eight energy levels are considered to be given by perturbed ABX energy levels.

TALLE 19. Perturbed energy levels ABK system.

$$1(x \neq x) = H_{1}$$

$$2(x \neq \beta) = H_{2} - \frac{\partial^{2}}{24} \Delta_{24} - \frac{\partial^{2}}{23} \Delta_{23}$$

$$3(x \neq x) = H_{3} + \frac{\partial^{2}}{23} \Delta_{23}$$

$$4(\beta \neq x) = H_{4} + \frac{\partial^{2}}{24} \Delta_{24}$$

$$5(x \neq \beta) = H_{5} - \frac{\partial^{2}}{57} \Delta_{57}$$

$$6(\beta \neq \beta) = H_{6} - \frac{\partial^{2}}{67} \Delta_{67}$$

$$7(\beta \neq x) = H_{7} + \frac{\partial^{2}}{57} \Delta_{57} + \frac{\partial^{2}}{67} \Delta_{67}$$

$$8(\beta \neq \beta) = H_{8}$$

where β represents the low energy state and \propto the high energy state. Thus the transitions are subject to changes as follows (Table 29) and the correlated values can be used for the ABX treatment and the process repeated to give accurate values of coupling constants and chemical shifts. The method appears to break down when any ($\frac{3}{2}/\Delta$) value is greater than about 5% of the J_{AB} coupling constant since this prevents the iteration procedure from converging.

d) <u>ABC</u> ABC treatments are difficult to apply. An iterative procedure can be used to obtain convergence of calculated and observed values. However for some molecules, two or more sets of parameters can be obtained which both fit

	1	·····		
	Atom with spin change	Transition	ABX Energy difference	ABK energy difference
1	В	8→6	E ₆ - E ₈	$(E_6 - E_8) - (\delta^2 / \Delta)_{67}$
2	В	7→4	E ₄ - E ₇	$(E_4 - E_7) + (\delta^2 / \Delta)_{24} - (\delta^2 / \Delta)_{57} - (\delta^2 / \Delta)_{67}$
3	В	5→2	E ₂ - E ₅	$(E_2 - E_5) + (\delta^2 / \Delta)_{57} - (\delta^2 / \Delta)_{24} - (\delta^2 / \Delta)_{23}$
4	В	3→1	E ₁ - E ₃	$(E_1 - E_3) - (\delta^2 / \Delta)_{23}$
5	A	8->5	E ₅ - E ₈	$(E_5 - E_8) - (\frac{5}{2}/\Delta)_{57}$
6	A	7→3	E ₃ - E ₇	$(E_3 - E_7) + (\delta^2 / \Delta)_{23} - (\delta^2 / \Delta)_{57} - (\delta^2 / \Delta)_{67}$
7	A	6->2	E ₂ - E ₆	$(E_2 - E_6) + (\delta^2 / \Delta)_{67} - (\delta^2 / \Delta)_{24} - (\delta^2 / \Delta)_{23}$
8	A	4->1	$E_1 - E_4$	$(E_1 - E_4) - (\delta^2 / \Omega)_{24}$
9	· K · ·	8-⇒7	E ₇ - E ₈	$(E_7 - E_8) + (\delta^2 / \Delta)_{57} + (\delta^2 / \Delta)_{67}$
10	к	5 -> ?	E ₃ - E ₅	$(E_3-E_5)+(\delta^2/\Delta)_{23}+(\delta^2/\Delta)_{57}$
11	к	6->.;	E ₄ - E ₆	$(E_4 - E_6) + (\delta^2 / \Delta)_{24} + (\delta^2 / \Delta)_{67}$
12	ĸ	2 -> 1	$E_1 - E_2$	$(E_1 - E_2) + (\partial^2 / \Delta)_{24} + (\partial^2 / \Delta)_{23}$
13	ABK	7	E ₂ - E ₇	$(E_2 - E_7) - (\partial^2 / \Lambda)_{24} - (\partial^2 / \Lambda)_{23}$
				$-(\partial^2/\Delta)_{57}-(\partial^2/\Delta)_{67}$
14	ABK	5 -⇒4	E E ₅	$(E_4 - E_5) + (\partial^2 / \Delta)_{57} + (\partial^2 / \Delta)_{24}$
15	ABK	6->3	E ₃ - E ₆	$(E_3 - E_6) + (\delta^2 / \Delta)_{23} + (\delta^2 / \Delta)_{67}$
			1	l

...

TABLE 20 Perturbed energy differences for calculation

Porturbed levels suitable for ABX calculation

the data⁶⁵. ABC treatment are discussed by Emsley, Feeney and Sutcliffe⁶⁵, In this work a simple iterative procedure has been used with limited success using a computer program (Appendix I).

The limitations of ABC treatments based purely on positions of resonance at one radiofrequency, are shown by the following results obtained during the study of methyl acrylate in carbon disulphide solution. The ratios of $\int J$ are quite small

$$\frac{\delta_{AB}}{J_{AB}} = \frac{14.7}{18.5}; \quad \frac{\delta_{BC}}{J_{BC}} = \frac{19.1}{11.3}; \quad \frac{\delta_{AC}}{J_{AC}} = \frac{33.8}{0.3};$$

$$- \frac{19.1}{J_{BC}} = \frac{19.1}{11.3}; \quad \frac{\delta_{AC}}{J_{AC}} = \frac{33.8}{0.3};$$

A series of values of chemical shifts and coupling constants were found to give acceptable spectra (see Table 21). Variations of up to 1.3 Hz in one coupling constant (with corresponding changes in other coupling constants) produced no change in the spectra. The conclusion from these figures is that values of coupling constants in ABC systems must be treated with care especially if conclusions are to be drawn from small changes in their values. The problems of obtaining accurate parameters from ABC spectra can be reduced by using two different operating radiofrequencies⁶⁷.

In ABK or ABC system, it is much simpler to produce a calculated spectrum from known values of coupling constants and chemical shifts than to obtain coupling constants and chemical shifts from an observed spectrum. To obtain a calculated spectrum a matrix representing the energy levels is constructed. This can be factorised into sub-matrices of

125 -

TABLE 21 Sets of parameters which fit the observed room

temperature spectrum of methyl acrylate (CS₂ sol^{n} .)

(illustrating the difficulties of determining accurate coupling constants from ABC spectra)

Set	1	2	3	4	5	6	7
JAB	18.5	13.4	18.4	18.1	18.0	18.0	17•9
J _{BC}	11.3	11.2	11.1	10.9	10.8	10.6	10.6
J _{AC}	0.3	0•4	0.6	1.1	1.3	1.5	1.6
V_{A}	42.6	42.6	42.6	42.9	42.9	42.9	43.0
$\nu_{\scriptscriptstyle B}$	27.9	27.9	27.9	27.9	27.8	27.9	27.8
\mathcal{V}_{c}	8.8.	8.8	8.7	8.6	8.5	8.4	8.4
Observe Spectra	d	Calcul	ated spec	tra usin	g the alc	ve sets of	parameters
	1	2	3	4	5	6	7
0.0	-0.01	0.07	0.02	0,02	-0.04	0,00	-0,03
4.3	4.29	4•34	4.31	4.29	4.24	4.28	4.25
9.1	9.10	9 .15	9.09	9.16	9.11	9.05	9.07
13.4	13.41	13.42	13.38	13.43	13.39	13.32	13.36
12.2	12.26	12.31	12.22	12.30	12.23	12,23	12.22
21.4	21.39	21.39	21.30	21.44	21.33	21,27	21.32
28.9 ^(B)	28.95	28,95	28.96	28.98	28.90	29.01	28.93
38.1	38.07	38.04	38.04	30.13	3 8.05	38.05	38.03
	·			Lanna and		l	A

Observed Spectra	, 1	2	3	4	5	6	7
36.9	3 6.94	36.92	36.85	36.98	36.92	36.87	36,92
41.2	41.25	41.20	41.14	41.25	41.20	41.14	41.20
53.6 (A)	53.62	53.57	53.5 9	53.67	53. 59	53.65	53.63
57•9	57.92	57.84	57.88	57 •94	57.07	57•93	57.91
28.9 (Comb)	28.96	23.95	28.94	28 .97	28 •93	28.92	28.96

Range of values of coupling constants which give acceptable spectra

 $J_{AB} = 17.9 - 18.5$ $J_{BC} = 10.6 - 11.3$ $J_{AC} = 1.6 - 0.3$

					• •		
H	0	0	0 .	0	0	0	0
0	^н 2	¹ / ₂ J _{BC}	¹ / ₂ J _{AC}	0	0	· 0	0
0	¹ /₂J _{BC}	н3	¹ ₂ J _{AB}	0	0	0	. 0
0	12JAC	¹ ₂ J _{AB}	^H 4	0	0	0	• 0
0	0	0	0	^H 5	¹ J _{AB}	JAC	0
0	0	0	U	¹ / ₂ J _{AB}	^н б	¹ ₂J _{BC}	0
0	0	0	0	1JAC	ל שני	H ₇	0
0	0	0	0	0	0	0	^H 8
-						1. 1	ل

size 1 by 1 (for total spin +3/2 and -3/2) and 3 by 3 (for total spin $+\frac{1}{2}$ and $-\frac{1}{2}$).

The roots and eigenvalues can be obtained by diagonalising the matrix and then the shift positions and intensities of the transitions can be calculated and compared with observed values.

In most compounds containing a vinyl group, at least an ABK treatment is necessary and more often an ABC treatment must be used.

3. <u>Other Spin Systems</u> The second order treatment of the other systems present in the molecules examined has not been studied in detail. The principles of the methods are similar. The number of transitions in a complex ABX₃ spectrum is forty four and for an ABCX system, fifty transitions including eighteen combination lines are possible.

- 128 -

TABLE 22. Treatments for other systems.

Molecule	Type of Treatment Necessary
Acraldehyde	ABCX
Trans-Crotonaldehyde	ABR ₃ X
Ethylideneacetone	ABX ₃ (and an uncoupled
	nethyl group)
Methyl <u>trans</u> -Crotonate	ABX ₃ (and an uncoupled
	methyl group)
Ethyl <u>trans</u> -Crotonate	ABX ₃ (and a simple
	A ₃ X ₂ ethyl group)

If a double resonance experiment is carried out, decoupling of interacting nuclei occurs, thus simplifying an otherwise -complex system. Saturation of the X protons in an ABX₃ system by irradiating at the frequency of the resonance of the X protons reduces the remaining spectra to a much simpler AB system. The technique is difficult to apply in an ABC system because of the closeness of the resonances.

In an AB system the coupling constant can be obtained direct from the spectrum.



The difference in chemical shifts can be calculated as $v_A - v_B = \int ((4-1)(3-2)^{-\frac{1}{2}}$ In the ABX₃ systems, ethylidenesseetone and <u>trans</u>-crotonate esters, the errors involved in using an AMX₃ approach are about 1 Hz in chemical shift of the A and B protons (the A and B protons in fact being closer together than the first order treatment predicts) and small errors of 0.2 Hz in the coupling constants. This chemical shift error was checked in the case of methyl <u>trans</u>-crotonate by a double resonance experiment and the error was found to be 0.9 Hz for both the A and B protons.

B TEMPERATURE AND SOLVENT STUDIES

Many of these molecules have been studied by other workers. Acraldehyde has been studied at 60 MHz⁶⁸ and 100 MHz¹²; in the latter study, some temperature dependence was observed for the chemical shifts (up to 11 Hz) of the vinyl protons although no appreciable change in coupling constants was detected. Although these shifts could be associated with changes in equilibrium position between two conformers, it seems more likely that these changes are caused by intramolecular and intermolecular interaction effects.

 (M°) values for acryoyl fluoride based on changes in an averaged chemical shift of the two conformers in rapid equilibrium have been calculated. The disorepancy between the enthalpy difference based on N.M.R. measurements³¹ ($\Lambda H^{\circ} = 800 \text{ cal mol}^{-1}$ (3.34 KJ mol⁻¹)), and microwave²⁹ and infrared³⁰ measurements ($\Lambda H^{\circ} = 100 \text{ cal mol}^{-1}(0.42 \text{ KJ mol}^{-1}))$ may be caused by changes in ohemical shifts with temperature, not associated with the <u>s-trans s-cis</u> equilibrium as in the case of shifts in temperature in vinyl halides⁶⁹ where no conformational equilibrium is possible. Trans-crotonaldehyde has














also been studied and discussed in the literature^{70,71}. Conflicting values for the N.M.R. parameters, particularly the coupling constants, have been reported by Castellano and Waugh⁷² and Brugel and coworkers⁷³ for methyl vinyl ketone presumably because of the complex ABC nature of the spectrum. The present work supports the results of Castellano and Waugh⁷². A number of $\alpha\beta$ -unsaturated ketones including methyl vinyl ketone and ethylideneacetone have been reported 'y Ronayne, Sargent and Williams²¹ both at room temperature and at several other temperatures. Methyl crotonates has been studied⁷⁴ as have certain acrylates⁷³.

Room temperature 60 mHz spectra of all these compounds were recorded. Detailed variable temperature studies were carried on methyl vinyl ketone, methyl acrylate, and methyl <u>trans</u>crotonat.. The spectra are illustrated in Figures 23 - 26.

The methyl vinyl ketone N.M.R. parameters are shown in Table 23. These results are similar to those of Ronayne, Sargent and Williams²¹. The changes with solvent at room temperature have been interpreted by these workers in terms of an equilibrium of the type

Aronatic Hydrocarbon + Ketone \rightleftharpoons Complex The changes with temperature have been interpreted in terms of both the equilibrium above and also the equilibrium between <u>s-trans</u> and <u>s-cis</u> conformers. It is clear that there is a very small coupling between the

 \propto hydrogen proton and the methyl protons, as no ringing is observed for the \propto proton absorbances but ringing is observed for the other vinyl protons (Figure 27).

TABLE 23 Methyl vinyl ketone parameters



a)	Liquid at room temp. Chemical Shifts (in Hz)	10% toluene solution at room temp.	Solvent shift	10% toluene solution at -60°C	Temperature Shift
$V_{\rm A}$	380.4	363.4	17.0	356.5	6.9
\mathcal{V}_{B}	375.1	344.1	31.0	3 28•4	15.7
Ъ	355•9	319•7	36.2	308.9	10.8
CH _z	134.0	109.6	24.4	114.7	-5.1
JAB	17,9	17.9 .		18.4	
JAC	10.9	10.7		11.7	
J _{BC} .	1.0	1.1		0.8	

b)	Toluene solutions					
	Roor	n Temp (3)	-60°C (d)		
a.	$\nu_{\rm A}$	$\nu_{\rm B}$	VC	$\nu_{\rm A}$	$\nu_{\rm B}$	VC
Present work 60mHz 21	6.06	5•73	5.33	5•94	5•47	5.15
Nef (as observed on graph) 100mHz	6.05	5•72	5.33	5198	5.49	5.20

N.B. Their concentrations are not quite the same as those of this work.

Ethylideneacetone has also been shown to be temperature dependent. Using a first order treatment (N.B. errors of about 1 Hz in v_A and v_B), the following values were obtained for neat ethylideneacetone at room temperature

 $v_A = 354 \text{ Hz}; J_{AB} = 16.0 \text{ Hz}; CH_3(C) H(A)$ $v_B = 405 \text{ Hz}; J_{BC} = 6.6 \text{ Hz};$ $v_C = 90 \text{ Hz}; J_{AC} = 1.4 \text{ Hz}; H(B) - C$ $v_D = 123 \text{ Hz}; \text{ other couplings zero}$

Ronayne, Sargent and Williams²¹ were able to relate the temperature dependent proton resonances of 3β -unsaturated ketones in toluene d⁸ solution to the presence of a predominate conformer. They concluded that methyl vinyl ketone and ethylideneacetone existed in predominantly the <u>s-trans</u> conformation using comparisons with other fixed <u>s-trans</u> and <u>s-cis</u> β -unsaturated ketones.

Methyl acrylate was investigated at various temperatures in carbon disulphide (Table 24).

The shifts were quite small and although they were compatible with an <u>s-cis</u> <u>s-trans</u> equilibrium they did not provide further information on conformations.

Methyl <u>trans</u>-crotonate revealed shifts with temperature. Using first order treatment and a double resonance experiment at room temperature the values in Table 25 were obtained.



	Solution in CS ₂ room temp (Hz)	Solution in CS ₂ -80 [°] C (Hz)
VA	377.6	374•7
VB	362.9	359.8
$\nu_{\rm c}$	343.8	344.9
∨ _{CH} 3	219	215
J _{AB}	18,5	17.1
J _{BC}	11.3	10.5
J _{AC}	0.3	1.1
Sum of coupling constants	30.1	28.5

TABLE 25 N.M.R. parameters of methyl trans-crotonate



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In the double resonance experiment, the methyl protons were irradiated and the remaining AB spectrum examined.

The ethyl esters were not investigated in detail but their room temperature spectra are listed in Table 26. (Figs. 27,28).

In all cases investigated, temperatures of -100° were reached in an attempt to obtain separate spectra for the two conformers. Unless a low enough temperature is reached to obtain separate spectra, N.M.R. can only provide supporting evidence for the existence of two conformers. The absence of two separate spectra shows that the barrier to rotation is low, and the interconversion of the two conformers is too fast to observe separate spectra on the relatively slow time scale of N.M.R. measurements compared with infrared.

- 143 -





.TABLE 26 N.M.R. parameters of ethyl acrylate and trans-crotonate



Parameters	'Hz
ν_{A}	378
$\nu_{\rm B}$	365
ν_c	345
$\mathcal{V}_{\mathtt{D}}$	248
$ u_{\rm E}$	75
\mathcal{J}_{AB}	18,2
J _{BC}	0.6
J _{AC} - 1	·6 _ 11.3
$\mathcal{J}_{\mathrm{DE}}$	7.0



Parameters	lst order treatment (Hz)
	345
$_{\mu} \nu_{\rm B}^{\rm A}$	414
$\nu_{\rm c}$	112
$\mathbf{v}_{\mathbf{D}}$ is	247
\mathcal{V}_{E}	75
JAB	16.0
J _{BC}	6.7
JAC	1.7
J	7.0

CHAPTER V

MASS SPECTROMETRY

A $\mathcal{A}\beta$ -Unsaturated Aldehydes and Ketones B $\mathcal{A}\beta$ -Unsaturated Esters The spectra of these compounds are shown as bar diagrams in Figures 2.9 to 36. Fragmentations were confirmed by observation of the appropriate metastable transitions wherever possible using a computer program (Appendix I). The mass spectral fragmentations of cyclic $\alpha\beta$ -unsaturated ketones⁷⁵ and esters⁷⁶ have been discussed, but the behaviour of acyclic $d\beta$ -unsaturated carbonyl compounds⁷⁷ has not received much attention. The aldehydes and ketones are discussed first.

A <u>*dB*-UNSATURATED</u> ALDEHYDES AND KETONES

The mass spectra of acraldehyde, <u>trans</u>-crotonaldehyde, methyl vinyl ketone and ethylideneacetone all showed a strong parent ion. In the aldehydes, an intense P-1 peak was observed whereas in the ketones the P-1 peak was less intense. This suggested that the aldehydic protons were more easily lost than the olefinic protons. It would be expected that an equivalent loss of a methyl group would occur in the ketones and this was confirmed by the appearance of strong P-15 peak. An ion of the form $[RCH=CH-C=0]^+$ in both cases could then lose CO to form strong peaks at m/e 27 and 41 depending on the



- 148 -





$$R^{1}=R^{2}=H;$$
 m/e 56 \rightarrow m/e 55 $\xrightarrow{m}13.25$ m/e 27
 $R^{1}=H, R^{2}=CH_{3};$ m/e 70 $\xrightarrow{m*68.01}$ m/e 69 $\xrightarrow{m*24.36}$ m/e 41
 $R^{1}=CH_{3}, R^{2}=H;$ m/e 70 \rightarrow m/e 55 $\xrightarrow{m*13.25}$ m/e 27
 $R^{1}=R^{2}=CH_{3};$ m/e 84 $\xrightarrow{m*56.67}$ m/e 69 $\xrightarrow{m*24.36}$ m/e 41
The suggestion that it was the methyl group which was lost
was supported by the ready cleavage of a molecule of CO
confirmed by the metastables. (Also by the loss of 29
corresponding to the ethyl group in ethyl vinyl ketone⁷⁸).
The $\left[CH_{3}CH=CH\right]^{+}$ ion of m/e 41 produced in \underline{trans} -croton-
aldehyde and ethylideneacetone could then lose 2 hydrogen
atoms and would give rise to an m/e 39 peak which could have
a cyclic structure.



The type of structure has been postulated for the $C_{3H_3}^+$ ion when it was formed in the mass spectrum of butadiene and pentadiene⁷⁹.

Major fragmentation occured when the C-C bond was broken. The charge could be retained by either grouping.



Since the R^2 -CH=CH grouping can also to produced by the two stage process already described, it was difficult to establish which fragment favoured charge retention. $R^1=R^2=H$; m/e 56 \rightarrow m/e 27 or m/e 29 (27 stronger) $R^1=H$; $R^2=CH_3$; m/e 70 \rightarrow m/e 41 or m/e 29 (41 stronger) $R^1=CH_3$, $R^2=H$; m/e 70 \rightarrow m/e 27 or m/e 43 (equal intensity) $R^1=R^2=CH_3$; m/e 84 \rightarrow m/e 41 or m/e 43 (41 stronger) Double bond migration was possible in compounds containing the ethylidene group. This has been observed in methyl esters of other $\not\prec\beta$ -unsaturated carbonyl compounds⁸¹ of the form



Migration could occur as illustrated below:-

 $\begin{bmatrix} CH_3 - CH = CH - CO - CH_3 \end{bmatrix}^+$ $\begin{bmatrix} CH_2 = CH - CH_2 - CO - CH_3 \end{bmatrix}^+$

Cleavage of the \measuredangle or β bonds to the vinyl group could then occur. The latter would proluce an m/e value which could be obtained by other routes. However, an intense peak at n/e 27 was only explicable in terms of cleavage of the rearrangement ion. This migration is well known for a number of $\alpha\beta$ -unsaturated carbonyl compounds with a β -methyl (e.g. mesityl oxide) under ordinary conditions and it was therefore not surprising that it could easily occur under the drastic conditions of electron impact.

$$CH_3 = CH_2CO_CH_3 \rightleftharpoons CH_2=C_2CH_2-CO_CH_3$$

B UNSATURATED ESTERS

The molecular ions of the esters were generally weaker than the aldehydes and ketones. The molecular ions of acrylates were weaker than those of the crotonates whereas the P-1 peaks were relatively intense compared with the crotonates. This suggested that a hydrogen was more easily lost from a vinylic grouping than from an ethylidene grouping.

Loss of a methyl radical appeared to occur readily from the ethylidene grouping in the esters since there were strong P-15 peaks in both crotonate esters and no P-15 was observed in methyl acrylate. This loss of a methyl radical was not very marked in <u>trans</u>-crotonaldehyde and could not be separated from a loss of the ketonic methyl group in ethylideneacetone. The base peak in the spectra of all four esters was produced either a) by cleavage of OR from the ester followed by loss of CO producing a peak for the $[RCH=CH]^+$ ion or b) by direct cleavage of the \measuredangle bond; in both cases in an analogous manner to the aldehydes and ketones.



 $\begin{array}{c} R^{1}=CH_{3}; \ R^{2}=H; \ m/e \ 86 \longrightarrow m/e \ 55 \) \\ R^{1}=C_{2}H_{5}; \ R^{2}=H; \ m/e \ 100 \longrightarrow m/e \ 55 \) \\ R^{1}=CH_{3}; \ R^{2}=CH_{3}; \ m/e \ 100 \ \underline{m^{*} \ 47.61} \\ R^{1}=C_{2}H_{5}; \ R^{2}=CH_{3}; \ m/e \ 114 \ \underline{m^{*} \ 41.76} \\ R^{1}=C_{2}H_{5}; \ R^{2}=CH_{3}; \ m/e \ 114 \ \underline{m^{*} \ 41.76} \\ m/e \ 69 \) \\ \end{array}$

- 153 -



FIGURE 34 MS2 70EV ETHYL ACRYLATE



154



155

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b) R's as above $m/e 86 \longrightarrow m/e 27 \text{ or } m/e 59$ $m/e 100 \longrightarrow m/e 27 \text{ or } m/e 73$ $m/e 100 \longrightarrow m/e 41 \text{ or } m/e 59$ $m/e 114 \longrightarrow m/e 41 \text{ or } m/e 73$

The m/e 41 peak in the crotonate esters could again lose two hydrogens to give the cyclic $C_{3H_{3}}$ ion. Double migration was again possible as in the aldehydes and ketones. Biemann⁸¹ has reported that it is possible for methanol to be eliminated in small amounts from the <u>trans</u>-methyl crotonate as a result of isomerisation of the trans molecular ion to the cis form. A small peak at m/e 68 supported this conclusion. A low intensity peak was also observed at m/e 68 in the spectrum of ethyl crotonate which could have been caused by the analagous loss of $C_{2H_{5}}$ OH on isomerisation of the molecular ion to the cis form. H



An alternative mechanism for eliminating alcohols from unsaturated esters by simple hydrogen migration from the <u>s-cis</u> form rather than by initial trans-cis isomerism is as follows:-

- 156 -



Deuteration studies might help in establishing which of these possibilities is correct. Peaks at m/e 68 and 82 in methyl and ethyl acrylate appeared to be caused by loss of water. The fragmentation process appeared difficult to establish. This process appeared to be much less favoured in the crotonate esters. Peaks at 42 and 58 in methyl acrylate suggested eliminations of CO_2 . The reason for the apparent easier elimination in methyl acrylate may be the greater facility of the following reaction.



R=H in methyl esters; R=CH₃ in ethyl esters

A peak at 86 in ethyl crotonate suggested the elimination of ethylene to give the acid ion. This reaction is apparently less favoured in ethyl acrylate. There was no evidence in any of these $\mathcal{A}_{\mathcal{B}}$ -unsaturated carbonyl compounds for McLafferty rearrangements⁷⁷ in confirmation of the observation that these would be suppressed in the presence of C=C. The spectra did indicate the existence of alkoxyl migrations of the type proposed



The lack of evidence for alkoxyl migration agreed with the contention that a β -phenyl substituent on the double bond was needed to facilitate the rearrangement. No evidence was found for <u>s-cis</u>, <u>s-trans</u> isomers which was consistent with a low energy barrier to rotation in relation to the energy associated with electron impact.

CHAPTER VI

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DISCUSSION OF RESULTS

The general trends in stability of s-trans and s-cis or non-planar conformers are illustrated in Table 27.

The present studies support the existence of acraldehyde and trans-crotonaldehyde in the s-trans conformation. The evidence is based on resolved vibrational fine structure and lack of variation in intensities of infrared bands with temperature in solution or vapour. These methods cannot readily detect conformers with additional enthalpies of more than 1 Kcal mo1⁻¹. (4.2 KJ mo1⁻¹) compared with the most stable form. This arises because the concentration of these higher enthalpy forms amounts to less than 1%. Ultrasonic methods are more suited to the determination of large AH^O values. Values of

> 2.66 cal mol⁻¹ (8.61 KJ mol⁻¹) and 1.93cal mol⁻¹ (8.07 KJ mol⁻¹) have teen

proposed¹⁰ for the excess enthalpy of the <u>s-cis</u> forms of acraldehyde and trans-crotonaldehyde respectively over the s-trans conformers. The present results are not inconsistent with the earlier ultrasonic measurements. The only case known in which detectable amounts of two conformers are observed in simple $\prec \beta$ -unsaturated aldehydes is in 2-furanaldehyde where the enthalpy difference is of the order of 1 Kcal mole $(4.2 \text{ KJ mole}^{-1})^{15}$.

The inherent stability of the s-trans conformers of $\prec \beta$ -unsaturated aldehydes can best be understood in terms of the repulsive forces between electrons in T-orbitals being a minimum in the s-trans conformer. The relative stability of the s-trans conformer of 2-furanaldehyde may be reduced by the aromatic nature of the furan ring, since the ring of

- 160 -

TABLE 27

General trends in stability in *AP*-unsaturated

carbonyl compounds

Ethylene grouping Group attached to carbonyl	Vinyl H H	trans- ethylidene CH H C=C	Vinylidene H H	$\frac{\frac{1}{2}risubstituted}{CH_{3}}C = C^{H}$
H aldehyde (1)	<u>s-trans</u>	<u>s-trans</u>	<u>s-trans</u>	?
CH ₃ ketone	(22) (19) Equilibrium mixture excess enthalpy of <u>s-cis</u> 	(19) Equilibrium mixture excess enthalpy of <u>s-cis</u> 20.5Kcal mol ⁻¹	<u>s-trans</u>	<u>s-cis</u> or non-planar
C2H5 ketone	(22) Equilibrium mixture excess enthalpy of <u>s-cis</u> <u>-0.1 Kcal</u> mol ⁻¹	Equilibrium Mixture	<u>s-trans</u>	<u>s-cis</u> or non-planar
CH(CH ₃) ₂ ketone	22) Equilibrium mixture	Equilibrium Mixture	<u>s-trans</u>	<u>s-cis</u> or non-planar
C(CH ₃)3	22) Equilibrium mixture	Equilibrium Mixture	<u>s-trans</u>	<u>s-cis</u> or non-planar

Comments (1) 2-furanaldehyde exists in detectable quantities of both <u>s-trans</u> and <u>s-cis</u> conformers

- (2) Enthalpies from variable temperature infrared studies
- (3) Increasing proportions of <u>s-cis</u> as larger ketone alkyl groups
- (4) Ringed figures refer to general references.

TABLE 27 (continued)

Ethylene	Vinvl	trans-	Vinvlidene	Trisubetituted
grouping		ethylidene	V INJ II GANG	
Group attached to carbonyl				
CH acid	Equilibrium Mixture (33) "Comparable proportions"	Equilibrium nixture	<u>s-trans</u>	n Storage Charles Storage Storage Storage Storage Storage Storage Storage Storage
OCH 3 ester	E.M. Excess enthalpy of <u>s-ois</u> <u></u>	E.M. Excess enthalpy of <u>s-cis</u> <u></u> 0.5 Kcal mol ⁻¹	<u>s-trans</u>	
OC ₂ H ₅ ester	E.M. Excess enthalpy of <u>s-cis</u> 	E.M. Excess enthalpy of <u>s-cis</u> <u>0.5 Kcal</u> mol ⁻¹	<u>s-trans</u>	?
F acid fluoride	29 30 31 E.M. Excess enthalpy of s-cis -0.1 Kcal mol ⁻¹) E.M.	<u>s-trans</u>	?
Cl acid chloride	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} $	(28) E.M.	<u>s-trans</u>	?
Br acid bromide	(28) E.M.	E.M.	<u>s-trans</u>	?

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- 162 -

E.M. Equilibrium Mixture

T -electrons can interact with the carbonyl electrons of either the <u>s-trans</u> or <u>s-cis</u> conformers, and there appears to be smaller repulsive forces between T -electrons in the <u>s-cis</u> form compared with acyclic systems. It is also possible that there is some repulsion between the lone pair electrons of the furan ring oxygen and the carbonyl oxygen in the <u>s-trans</u> conformer.

From these studies and other earlier studies¹⁹, it is clear that the replacement of the aldehydic hydrogen by an alkyl group can shift the position of equilibrium towards the <u>s-cis</u> conformer. From the variable temperature infrared solution and vapour studies, methyl vinyl ketone and ethylideneacetone exist in an equilibrium mixture in which the <u>s-cis</u> conformer has an excess enthalpy of about 0.5 Kcal mole⁻¹ (2.1 KJ mole⁻¹).

In general, $\prec \beta$ -unsaturated ketones appear to exist in an equilibrium mixture when there are trans hydrogens (i.e. $R^2=R^3=H$); on the ethylenic double bond. R^1 has little influence on the



position of equilibrium as might be expected, since R^1 is remote from the part of the molecule involved in conformational change.

For larger alkyl substituents \mathbb{R}^4 , the <u>s-cis</u> or non-planar conformer becomes more favoured. This result has been reported qualitatively for a series of vinyl ketónes²² and is supported by measurements⁷⁸ of $\triangle \mathbb{H}^0$ between the two conformers of ethyl vinyl ketone ($\Delta H^{\circ} = 124\pm60$ cal mol⁻¹ (518\pm251 J mol⁻¹)) in carbon disulphide solution in the temperature range -110° to 40° which is much lower than the value for methyl vinyl ketone ($\Delta H^{\circ} = 461\pm23$ cal mol⁻¹ (1.93\pm0.10 KJ mol⁻¹)) measured under similar conditions. This can be understood in terms of increasing repulsion between the β -hydrogen (R²) and the alkyl group, as molecules with larger alkyl groups (R⁴) are considered.

The molecule appears to exist entirely in the <u>s-trans</u> conformer in $\cancel{\beta}$ -insaturated ketones with an $\cancel{\beta}$ alkyl group (R³). This is probably because there will be a large steric repulsion between this alkyl group and the keto-alkyl group (R⁴) in the <u>s-cis</u> conformation.

The molecule appears to exist entirely in the <u>s-cis</u> or non-planar forms when \mathbb{R}^2 is an alkyl group as in mesityl oxide. In this case, there will be a large $\mathbb{R}^2 - \mathbb{R}^4$ sterio repulsion in the <u>s-trans</u> rolecules. In molecules in which \mathbb{R}^2 , \mathbb{R}^3 and \mathbb{R}^4 are all alkyl groups a non-planar form is very likely since there will be large repulsive interactions in both planar forms.

In $\mathcal{A}\beta$ -unsaturated esters, it would appear that a similar equilibrium exists between <u>s-cis</u> and <u>s-trans</u> confermers. The present work suggests that an equilibrium exists in methyl acrylate, ethyl acrylate, methyl <u>trans</u>crotonate, and ethyl <u>trans</u>-crotonate. The variable temperature infrared solution studies suggest that there is a slightly lower enthalpy difference compared with the corresponding ketones. It also appears that methacrylates and 3.3.dimethylacrylates exist in only one detectable conformation. It is assumed that methacrylates are <u>s-trans</u> and 3.3.dimethylacrylates are almost completely <u>s-cis</u> or non-planar.

Steric repulsion cannot completely explain all the results obtained in the present work and other studies. In acryoyl fluoride, the repulsion between the β -hydrogen and the fluorine in the <u>s-trans</u> must be extremely small. However the enthalpy difference between the two conformers^{29,30} is much smaller than the corresponding enthalpy difference in methyl vinyl ketone where larger repulsion would be expected in the <u>s-trans</u> conformer. There may be due to internal hydrogen bonding in both conformations, and presumably it is stronger in the <u>s-cis</u> conformer as this appears to be stabilised relative to the <u>s-trans</u> conformation.

In an equilibrium of this nature with small enthalpy differences and low barriers to rotation, it is clear that variable temperature infrared studies are appropriate. In certain cases, where nuclei are in very different environments (i.e. large chemical shift differences) or the energy barrier between conformers is large, nuclear magnetic resonance methods can be very effective since separate spectra can be observed for the two conformers. In these molecules, the rate of interconversion of the conformers in the systems studied is slower evidently faster than the time scale of a vibrational transition, Faster but slower than the time scale of an N.M.R. transition. This is consistent with the observation of certain infrared bands corresponding to the two conformers, whereas only an averaged N.M.R. spectrum is observed.

It has been suggested that the averaged position of chemical shifts can be related to conformational equilibrium^{21,31} in these and related systems. However, small changes in chemical shifts observed in these systems even at low temperature, corresponding to changes in the averaged spectrum, cannot be easily related to thermodynamic data or used to establish the existence of a conformational equilibrium because shifts with temperature can be attributed to solvent and environmental effects.

Mass spectrometry is very unlikely to aid in the detection of conformers unless the barrier to rotation is extremely high. However it can be used to characterise these molecules.

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APPENDICES

APPENDIX I

Computer Programs

APPENDIX II

Statistical Analysis of Results

APPENDIX III

Short Courses (1966 - 1969)
APPENDIX I Computer programs

Several computer programs have been written using the ALGOL 60 computing language. The relevant programs are shown in the pages following. Certain procedures used in these programs were provided by the Computer Unit staff at Kingston College of Technology. These procedures are AXESON, DLINE, JACOBI, KEY(X), DIRECTSEARCH.

The programs written are



ABCNMR;

```
"HEGIN" "REAL" WI, W2, W3, J12, J13, J23, E1, E8,
   SUM:
   "INTEGER" J, K, L, JJ, KK;
"DEGIN" "REAL" "ARRAY" H, U, HH, UU, FMULT[1:3,
      1:3], DEIGEN, SUMSQ[1:15];
      "FOR" Jt=1 "STEP" 1 "UNTIL" 3 "DO"
      "DEGIN" "FIR" K:=1 "STEP" 1 "UNTIL" 3 "DO"
         FMULT[J, K]:=1.0;
      "END";
      FMULT[1,
               3]:=FMULT[2, 2]:=FMULT[3, 1]:=0.0;
      "READ" W1, W2, W3, J12, J13, J23;
      E1:=0.5*(W1 + W2 + W3) + 0.25*(J12 + J13 + J23):
      E8:= -0.5 \neq (W1 + W2 + W3) + 0.25 \neq (J12 + J13 + J23);
      H[1, 1]:=0.5*(W1 + W2 - W3) + 0.25*(J12 - J23 - J13)
      H[2, 2]:=0.5*(W_{-} - W_{2} + W_{3}) + 0.25*( - J_{12} - J_{23} + J_{33})
      J.3);
      H[3, 3]:=0.5*(-W1 + W2 + W3) + 0.25*(-J12 + J23)
      - J13);
      H[1, 2]:=H[2, 1]:=0.5*J23;
      H[1, 3]:=H[3, 1]:=0.5*J13;
                                     and the second second second
      H[2] 3]:=H[3, 2]:=0.5*J12;
      "CLEMMENT" PROCEDURE CALL;
JACCBI(H, U, 3, 0.000001);
                                        · · · · ·
      HH[1, 1]:=0.5*(W1 - W2 - WS) + 0.25*( - J12 + J23 - J12 + J23)
      J13);
      HE[3, 2]:=0.5*(-W1 + W2 - W3) + 0.25*(-J12 - J23)
      + J13);
      HH[3, 3]:=0.5*(-W1 - W2 + W3) + 0.25*(J12 - J23 - J23)
      J13);
     HH[1, 2]:=HH[2, 1]:=0.5*J12;
HH[1, 3]:=HH[3, 1]:=0.5*J13;
HH[2, 3]:=HH[3, 2]:=0.5*J23;
      "COMMENT" PROCEDURE CALL;
      JACCBI(HH, JU, 3, 0.000001);
      "FCR" J:=1 "STEP" 1 "UNTIL" 3 "DO"
      "BEGIN" DEIGEN[J]:=E1 - H[J, J];
         SUM:=0.0;
         "FOR" K:=1 "STEP" 1 "UNTIL" 3 "DO" SUM:=SUM
         + U[K, J];
       · SUMSQ[J]:=SUM*SUM;
      "END":
      L:=3;
      "FUR" JI=1 "STEP" 1 "UNTIL" 3 "DO"
      "BEGIN" "FOR" K:=1 "STEP" 1 "UNTIL" 3 "DO"
         "DEGIN" L:=L + 1;
            DEIGEN[L]:=H[J, J] - HH[K, K];
            SUM:=0.0:
            "FCR" JJ:=1 "STEP" 1 "UNTIL" 3 "DO"
            "BEGIN" "FOR" KK:=1 "STEP" 1 "UNTIL" 3
               "DO" · SUM:=SUM + U[JJ, J]*UU[KK,
               k]*FMULT[JJ, KK];
            "END":
            SUMSQ[L]:=GUM*SUM
         "END":
      "END";
```

```
"FUR" J:=1 "STEP" 1 "UNTIL" 3 "DO"

"BEGIN" L:=J + 12;

DEIGEN[L]:=HH[J, J] - E3;

SUM:=0.0;

"FUR" K:=1 "STEP" 1 "UNTIL" 3 "DO" SUM:=SUM

+ UU[K, J];

SUMSQ[L]:=SUM*SUM

"END";

"FCR" L:=1 "STEP" 1 "UNTIL" 15 "DO"

"BEGIN" "PRINT" DIGITS(2), L, PREFIX(``),

ALIGNED(3, 2), DEIGEN[L], PREFIX(``),

ALIGNED(2, 2), SUMSQ[L];

"END";
```

"END":

ABCREP: "BEGIN" "REAL" SUM, ZEXP, DDELTA, SFSI, RHO, DELTA, R, JS, TI, T2, T3, Z; "INTEGER" J, JJ, K, KK, L, P1, P2, MAXEVAL; "REAL" "ARRAY" W, PSI[1:3], H, HH, U, UU, FMULT[1:3, 1:3], DEIGEN, SUMSQ, CBS[1:15]; "DOULEAN" CONVERGE; "PROCEDURE" JACODI(A, S, N, RHO); Corrected and the second "INTEGER" N; "REAL" RHO; "REAL" "ARRAY" A, S; "DEGIN" "REAL" NURMI, NURM2, THR, MU, CMEGA, SINT, COST, INTI, VI, V2, V3; "INTEGER" I, J, P, G, IND; "F(R" I:=1 "STLP" 1 "UNTIL" N "DO" "FOR" J:=1 "BTEP" 1 "UNTIL" I "DO" "IF" I = J "THEN" S[I, J]:=1.0 "ELSE" S[I, J]:=S[J, I]:=0.0; INT1:=0.0; ·.... "FIR" 'It=2 "STEP" 1 "UNTIL" N "DO" "FIR" Jt=1 "STEP" 1 "UNTIL" I - 1 "DO" INTI:=INTI + 2.0*A[I, J]†2; NLRM1:=SQRT(INT1); NORM2:=(RHO/N) *NORM1; THR:=NRM1; IND:=0; MAIN: THR:=THR/N: MAINLY "FOR" 'Q1=2 "STEP" 1 "UNTIL" N "DO" "FOR" I == "EP" 1 "UNTIL" Q - 1 "DO" "IF" ABS(A[P, Q]) "GE" THR ""THEN" "BEGIN" IND:=1: V1:=A[P; P]; V2:=A[P, Q]; V3:=A[G, Q]; MU:=0.5*(V1 - V3); CMEGA;="IF" MU = 0.0 "THEN" - 1.0 "ELSE" -SIGN(MU) *V2/SQRT(V2†2 + MU†2);

.

SINT:=LMEGA/S/RT(2.0*(1.0 + SQRT(1.0 - CMEGA(2)));COST:=5411(1.0 - SINT(2); "FCR" I;=1 "STEP" 1 "UNTIL" N "DO" "BEGIN" "IF" I "NE" F "AND" I "NE" ("THEN" "BEGIN" INT1:=A[I, P]; MU:=A[I, 4]; A[0, I]:=A[I, Q]:=INT1*SINT + MU*COST;A[P, I]:=A[I, P]:=INT1*CUST - MU*SINT; "END"; INT1:=S[I, P]; $MU_{1}=S[1, 4];$ S[I, 4]:=INT1*SINT + MU*COST; S[I, P]:=INT1+COST - MU+SINT; "END": A[P, P]:=V1*COST12 + V3*SIN112 - 2.0*V2*SINT*COST; A[9, 4]:=V1*SINT12 + V3*COST12 + 2.0*V2*SINT*COST: $A[P, 4]_{=}A[Q, P]_{=}(V1 - V3)*SINT^COST +$ V2*(COST13 - SINT12) "END"; "IF" IND = 1 "THEN" "BEGIN" IND:=0; "GOTO" MAIN1 "END" "ELSE" "IF" THE > NURM2 "THEN" "GOTO" MAIN "END" JACOBI; "KEAL" "FROCEDURE" ADC (PSI, H, HH, U, UU, DE IGEN, W); "REAL" "ARRAY" PSI, H, HH, U, UU, DEIGEN, W; "BEGIN" "REAL" E1, E3; "IN FEGER" J. K. L; E1:=0.5*(W[1] + W[2] + W[3]) + 0.25*(PSI[1] + PSI[2])+ PSI[3]);B8:= -0.5*(W[1] + W[2] + W[3]) + 0.25*(PSI[1] +SI[2] + PSI[3]);H[1, 1]:=0.5*(W[1] + W[2] - W[3]) + 0.25*(PSI[1] - W[3]) + 0.25*(PPSI[2] - PSI[3]);H[2, 2]:=0.5*(W[1] - W[2] + W[3]) + 0.25*(- PSI[1])+ PSI[2] - PSI[3]);H[3, 3];=0.5*(- W[1] + W[2] + W[3]) + 0.25*(-PSI[1] - PSI[2] + PSI[3]);H[1, 2]:=H[2, 1]:=0.5*PSI[3]; H[1, 3]:=H[3, 1]:=0.5*PSI[2]; H[2, 3]:=H[3, 2]:=0.5*PSI[1]; JACO31(H, U, 3, 0.000001); HH[1, 1] := 0.5 * (W[1] - W[2] - W[3]) + 0.25 * (- PBI[1])- PSI[2] + PSI[3]);HH[2, 2]:=0.5*(-W[1] + W[2] - W[3]) + 0.25*(-PSI[1] + PSI[2] - PSI[3]);HH[3, 3]:=0.5*(-W[1]-W[2]+W[3])+0.25*(PSI[1])- PSI[2] - PSI[3]);HH[1, 2];=HH[2, 1]:=0.5*PSI[1]; 3];=HH[3, 1];=0.5*P81[2]; HH[1, HH[2, 3];=HH[3, 2]:=0.5*PSI[3]; JACUBI(HH, UU, 3, 0.000001);

```
"FOR" J:=1 "STEP" 1 "UNTIL" 3 "DO"
   DEIGEN[J] := E1 - H[J, J];
   L:=3;
         J:=1 "STEP" 1 "UNTIL" 3 "DO" "FOR" K:=1
   "FOR"
   "STEP" 1 "UNTIL" 3 "DO"
   "BEGIN" L:=L + 1;
      DEIGEN[L]:=H[J, J] - HH[K, K];
   "END";
   "FOR" J:=1 "STEP" 1 "UNTIL" 3 "DO"
   "BEGIN" L:=J + 12:
      DSIGEN[L]:=HH[J, J] - E8
   "END":
"END";
"BOOLEAN" "PROCEDURE" KEY(I):
"VALUE" I;
"INTEGER" I:
"BEGIN" "CUDE"
   %LDR$1
   LD:1$1
   %SUBR:L$1
   %JZ$ZERO
   %RTOK
   %SML
   $$ZERU$ST$I
   %CTOM
   %AND$I
   %ST$I
            1.1
   LETI=I "NE" O
"END" KEY;
"REAL" "PROCEDURE" RDEV (PSI, H, HH, U, UU,
DEIGEN, LIBS, W, R);
"REAL" "ARRAY" PSI, H, HH, U, UU, DEIGEN, W,
CODS:
"REAL" R;
                                                      "BEGIN" ABC(PSI, H, HH, U, UU, DEIGEN, W);
  R_{i} = DEIGEN[1] - DEIGEN[7] - OBS[1] + OBS[7] +
  DEIGEN[2] - DEIGEN[4] - CDS[2] + CDS[4] + DEIGEN[11]
   - DEIGEN[15] - ODS[11] + ODS[15] + DEIGEN[12] -
  DEIGEN[14] - OBS[12] + OBS[14];
  R_{:=}R/4_{0};
"END":
"REAL" "PROCEDURE" TDEV (PSI, H, HH, U, UU,
DEIGEN, UDS, W, T1, T2, T3);
"REAL" "ARRAY" PSI, H, HH, U, UU, DEIGEN, ODS,
W:
"REAL" T1, T2, T3;
"BEGIN" ADC(PSI, H, HH, U, UU, DEIGEN, W);
   T1:=DEIGEN[3] + DEIGEN[5] + DEIGEN[9] + DEIGEN[13] -
UBS[3] - ODS[5] - OBS[9] - ODS[13];
  T1:=T1/4.0;
   T2:=DEIGEN[2] + DEIGEN[4] + DEIGEN[12] + DEIGEN[14] =
  ODS[2] = ODS[4] = ODS[12] = ODS[14];
```

```
T2:=T2/4.0;
    T3:=DEIGEN[1] + DEIGEN[7] + DEIGEN[11] + DEIGEN[15] -
    ODS[1] - ODS[7] - ODS[11] - ODS[15];
    T3:= T3/4_0:
"END";
"REAL" "PROCEDURE" ZDEV(PSI, H, HH, U, UU,
DEIGEN, UBS, W, Z);
"REAL" "ARRAY" FSI, H, HH, U, UU, DEIGEN,
                                                   CBS,
 W:
"REAL" Z:
 "BEGIN" "INTEGER" J:
    ABC(PSI, H, HH, U, UU, DEIGEN,
                                         W);
    Z1=0.0;
    "FOR" JI=1 "STEP" 1 "UNTIL" 15 "DO"
    "BEGIN" Z:=Z + ABS(DEIGEN[J] - OBS[J]);
       "PRINT" ALIGNED(3, 3), DEIGEN[J];
    "END":
    Z_1=Z - ABS(DEIGEN[6] - ODS[6]) - ABS(DEIGEN[8] - ABS(DEIGEN[8]))
    CBS[8]) - ABS (DEIGEN[10] - CBS[10]);
"END":
 "REAL" "PROCEDURE" SS(PSI);
"ARRAY" PSI;
"DEGIN" "REAL" G, F;
    "INTEGER" M;
   ABC(ISI, H, HH, U, UU, DEIGEN, W);
F:=ABS(PSI[1] + PSI[2] + PSI[3] - JS);
    "IF" F "GE" 0.2 "THEN" Q:=500.0 + 100.0*(F - 0.2)
    "ELSE"
                                           1.
    <sup>11</sup>DEGIN<sup>11</sup> C3=0.0;
      "FUR" M:=1 "STEP' 1 "UNTIL" 15 "DO" Q:=Q -
      ABS(DEIGEN[M] - OBS[M])
   "END";
   "IF" Q "LE" 400.0 "THEN".
   "BEGIN" Q:=Q - ABS(DEIGEN[6] - OBS[6]);
      C_1=Q - ADS(EIGN[8] - ODS[8]);
      Q_1=Q_2 - ABS(DEIGEN[10] - CBS[10]);
   "END";
   85: =Q;
   "IF" KEY(1) "THEN" "PRINT" PUNCH(3), SAMELINE,
"L'PSI, PSI[1], ", PSI[2], SS, Q;
"END";
"PROCEDURE" DIRECT SEARCH(PSI, KK, SPSI, DDELTA,
RHO, DELTA, CLINVERGE, MAXEVAL);
"VALUE" KK, DDELTA, RHD, DELTA, MAXEVAL;
"INTEGER" KK, MAKEVAL;
"ARRAY" PSI;
"REAL" DDELTA, RHO, DELTA, SPSI;
"BODLEAN" CONVERGE;
           ACM ALGORITHM 178;
"COMMENT"
"DEGIN" "INTEGER" K, EVAL;
   "ARRAY" THI, 5[1 : KK];
  "REAL" SPHI, SSSS, THETA;
  " "TROCEDURE" E;
 "FOR" K1=1 "STEP" 1 "UNTIL" KK "DO"
   "BEGIN" IHI[K] := PHI[K] + S[K];
```

- 179 -

EXIT: "END" LF DIRECT SEARCH;

"IF" SSSS "GE" SPSI "THEN" "GOTO" LI; "FOR" K:=1 "STEP" 1 "UNTIL" KK "DO" " ADS(PHI[K] - PSI[K]) > C.5*ADS(S[K]) "THEN" "GOTO" L2 "END"; L3: "IF" DDELTA "GE" DELTA "THEN" "BEGIN" DDELTA:=RHO*DDELTA; "FOR" K:=1 "STEP" 1 "UNTIL" KK "DO" S[K]:=RHO*S[K]; "GOTO" L1 "END";

"BEGIN" CUNVERGE:="FALSE"; "GOTO" EXIT: "END"; "FIR" KI=1 "STEP" 1 "UNTIL" KK "DO" "DEGIN" "IF" PHI[K] > PSI[K] "EQUIV" S[K] < 0"THEN" S[K] := - S[K]: THETA:=FSI[K]: PSI[K]:=PHI[K]; PHI[K]:=2.0*PHI[K] - THETA "END"; SPSI:=SSSS; SSSS:=SPHI:=SS(DHI); EVAL:=EVAL + 1; Ε; "IF" SSSS "GE" SPSI "THEN" "GOTO" LI; "FCR" KI=1 "STEP" 1 "UNTIL" KK "DO" "IF" $ABS(PHI[K] - PSI[K]) > C_5 * ABS(S[K])$ "THEN"

S[K]:=DDELTA; SPSI:=SS(ISI); EVAL:=1; CONVERGE:=""TR E"; L1: SSSS:=SPSI; "FUR" K:=1 "STEP" 1 "UNTIL" KK "DO" PHI[K]:=PSI[K]; E; "IF" SSSS < SPSI "THEN" "DEGIN"

"IF" EVAL "GE" MAXEVAL "THEN"

L2:

START: "FOR" KI=1 "STEP" 1 "UNTIL" KK "DO"

```
SPH1:=SS(1-H1);
EVAL:=EVAL + 1;
"IF" SPHI < SSSS "THEN" SSSS:=SPHI "ELSE"
"HEGIN" S[K]:= - S[K];
PHI[K]:=PHI[K] + 2.0*S[K];
SPH1:=SS(I-H1);
EVAL:=EVAL + 1;
"IF" SPHI < SSSS "THEN" & $$$$:=SPHI "ELSE"
IHI[K]:=PHI[K] - S[K];
"END";
```

- 181 -

"READ" W[1], W[2], W[3], PSI[1], PSI[2], PSI[3], JS, P1, P2, ZEXP, DDELTA, RHO, DELTA, MAXEVAL; "FUR" J:=1 "STEP" 1 "UNTIL" 15 "DO" "READ" CBS[J]; START: "FIR" J:=1 "STEP" 1 "UNTIL", F1 "DO" "BEGIN" RDEV (PSI, H, HH, U, UU, DEIGEN, ODS, W, R); PSI[3] = PSI[3] - R;"END": ZDEV(ISI, H, HH, U, UU, DEIGEN, OBS, W, Z); "PRINT" PUNCH(3), BEFORE DIRECTSEARCH ; "PRINT" PUNCH(3), ALIGNED(1, 3), Z; DIRECT SEARCH (PSI, 3, SPSI, DDELTA, RHD, DELTA, CUNVERGE, MAKEVAL); "IF" CUNVERGE "THEN" "PRINT" PUNCH (3), CONVERGE "ELSE" "IRINT" PUNCH(3), DID NOT CUNVERGE ; "PRINT" ALIGNED(2, 2), PSI[1], PSI[2], PSI[3], W[1], W[2], W[3], SPS1; "FCR" J:=1 "STEP" 1 "UNTIL" F2 "DO" "DEGIN" TDEV (ISI, H, HH, U, UU, DEIGEN, CDS, W, T1, T2, : T3); W[1]:=W[1] - T1; W[2]:=W[2] - T2;W[3]:=W[3] - T3;"END"; ZDEV (FSI, H, HH, U, UU, DEIGEN, CDS, W, Z); "IF" KEY(2) "THEN" ZEXP:=SPSI; "IF" Z "LE" ZEXP "THEN" "PRINT" ALIGNED(3, 2), W[1], W[2], W[3], PSI[1], PSI[2], PSI[3] "ELSE" "GOTO" START: "FOR" J:=1 "STEP" 1 "UNTIL" 15 "DO" "PRINT" ALIGNED(2, 2), DEIGEN[J], UBS[J]; "END";

·....

SHAPEA: "BEGIN" "REAL" Z, SCX, SCY, CGX, CGY, MX, MY, MO, MXX, MXY, MYY, MZZ, MXZ, MYZ, F, G, W, FI, XA, XB, YA, YB; "INTEGER" N, D, S, J; N:=D:=12; S;**≡14**; "BEGIN" "REAL" "ARRAY" X[1 : N], Y[1 : N], DO[1 : D], T[1:5], M[1:N], ST[1:3, 1:3]; "COMMENT" REQUIRES PROCEDURES AXESON, JACOBI, and DLINE; "FOR" J:=1 "STEP" 1 "UNTIL" D "DO" "READ" . . . * . Ex DO[J]: "FOR" J:=1 "STEP" 1 "UNTIL" S - 2 "DO" "READ" T[J]; "FOR" JI=1 "STEP" 1 "UNTIL" N "DO" "READ" MJI: Z:=180.0/3.14159265; "READ" F, G, W; ONCE: "IF" M[1] = 0.0 "THEN" "BEGIN" X[1]:=X[2]:=0.0; 1. Y[1]:=Y[2]:=10.0 "END"; "IF" M[1] "NE" 0.0 "THEN" "BEGIN" X[1]:=0.0; Y[1]:=10.0; X[2]:=X[1] + DO[2]*(CDS(T[2]/Z));Y[2]:=Y[1] + DO[2]*(SIN(T[2]/Z))"END"; "FOR" J:=3 "STEP" 1 "UNTIL" 12 "DO" "BEGIN" "IF" J = 6 "OR" J = 9 "THEN" "BEGIN" X[J] := X[J - 3] + DO[J] * (COG(T[J]/Z));Y[J]:=Y[J - 3] + DO[J]*(SIN(T[J]/Z))"END" "ELSE" "IF" J = 11 "THEN" "BEGIN" X[J] = X[J - 2] + DU[J] = (CUS(T[J]/2));= Y[J] := Y[J - 2] + DU[J] * (SIN(T[J]/Z))"END" "ELSE" "BEGIN" X[J]:=X[J - 1] + DO[J]*(COS(T[J]/Z)); Y[J]:=Y[J - 1] + DO[J]+(SIN(T[J]/Z))"END" "END": MX:=X[6] - 5.0; $MY_{=}Y[6] = 5.0;$ "FOR" J:=1 "STEP" 1 "UNTIL" 12 "DO" "BEGIN", X[J]:=X[J] - LX; Y[J]:=Y[J] - MY"END": Ά, AXESON(10, 0, 10, 0, SCX, SCY, **A**):

```
"IF" M[1] "NE" 0.0 "THEN"
"BEGIN" MOVEPEN(X[1]*SCX, Y[1]*SCY);
   CENCHAR(3):
   DRAWLINE (X[2]+SCX, Y[2]+SCY);
"END":
MOVEPEN(X[2]*SCX, Y[2]*SCY);
CENCHAR(3);
"FOR" J:=3, 4 "DO"
"BEGIN" DRAWLINE (X[J]*SCX, Y[J]*SCY);
   CENCHAR(3)
"END";
"IF" M[5] "NE" 0.0 "THEN"
"BEGIN" DRAWLINE(X[5]*6CX, Y[5]*5CY);
   CENCHAR(3):
"END":
MOVEPEN(X[3]*SCX, Y[3]*SCY - 5);
DRAULINE (X[6] + SCX, Y[6] + SCY - 5);
                   Y[6]*&CY + 5);
MIVEPEN(X[6]*SCX,
DRAYLINE (X[3]*SCX, Y[3]*SCY + 5);
MUVEPEN(X[6]*SCX, Y[6]*SCY);
CENCHAR(3);
DRAWLINE (X[7]*SCX, Y[7]*SCY);
CENCHAR (3);
"IF" M[8] "NE" 0.0 "THEN"
"BEGIN" DRAWLINE (X[8]*SCX, Y[8]*SCY);
   CENCHAR(3)
"END":
MOVEPEN(X[6]*SCX, Y[6]*SCY);
DRAWLINE(X[9]*SCX, Y[9]*SCY);
CENCHAR(3);
MOVEPEN(X[9]*SCX, Y[3]*SCY + 5);
DRAWLINE(X[10]*SCX, Y[10]*SCY + 5);
MOV2PEN(X[10]*SCX, Y[10]*SCY);
CENCHAR(3):
MIVEPEN(X[10]*SCX, Y[10]*SCX - 5);
DRAWLINE(X[9]*SCX, Y[9]*SCY - 5);
MOVEPEN(X[9]*SCX, Y[9]*SCY);
DRAWLINE (X[11]*SCX, Y[11]*SCY);
CENCHAR(3);
"IF" M[12] "NE" 0.0 "THEN"
"BEGIN" DRAWLINE(X[12]*SCX, Y[12]*SCY);
   CENCHAR(3)
"END";
MX := MY := MU := C . 0;
"FLR" J:=1 "STEP" 1 "UNTIL" N "DO"
"BEGIN" MX: MX + M[J] * X[J];
   MY_{1=MY} + M[J]*Y[J];
   MO_1 = MU + M[J]
"END";
CGX:=MX/MU;
CGY:=MY/MU;
MOVEPEN(CGX*SCX, CGY*SCY);
CENCHAR(1);
```

```
MXX:=MXY:=MYY:=MZZ:=MXZ:=MYZ:=0.0;
      "FOR" J:=1 "STEP" 1 "UNTIL" N "DO"
      "BEGIN" X[J]:=X[J] - CGX;
         Y[J] := Y[J] - CGY;
         MXX:=MXX + M[J]*X[J]*X[J];
         MYY:=MYY + M[J]*Y[J]*Y[J];
         MZZ:=MXX + MYY;
         MXY:=MXY + M[J]*X[J]*Y[J]
      "END";
      MXX:=MXX + W+0.89+0.89+2.0+1.008;
      MYY:=MYY + W*0.89*0.89*2.0*1.008;
      "BEGIN" "REAL" "ARRAY" A[1:3, 1:3];
         A[1,
              1]:=MYY;
         A[2, 2]:=MXX;
         A[3,
              3]:=MZZ;
         A[1,
               3]:=A[3,
                        1]:=F;
              3]: A[3, 2]:=G;
1]:=A[1, 2]:= - MXY;
         A[2,
         A[2,
         JACUBI (A, ST, 3, 0.000001);
       "PRINT"
MI ABOUT XYZ AXES
    MXX, MYY, MZZ;
        "PRINT"
PRINCIPAL MI
         1], A[2,
                     2], A[3, 3];
 , A[1,
        J_{1}=SIGN(2,0+MXY/(MXX - MYY));
         FI:=ARCTAN(ABS(2.0*MXY/(MXX - MYY)));
         FI:=FI*Z;
         "IF" J = 1 "THEN" T[13]:=F1/2.0 "ELSE"
         T[13]:=90.0 - FI/2.0;
         T[14]:=T[13] + 90.0;
         "FOR" J:=13 "STEP" 1 "UNTIL" 14 "DO"
         "BEGIN" XA:=CGX + 3.0*(COS(T[J]/Z));
            YA:=CGY + 3.0*(SIN(T[J]/Z));
            XB:=CGX - 3_0*(CDS(T[J]/Z));
            YB:=CGY - 3.0*(SIN(T[J]/Z));
            DLINE (XA*SCX, YA*SCY, XB*SCX, YB*SCY)
         "END";
         A[1, 1]:=A[1, 1]*1.660247;
         A[2, 2]:=A[2, 2]+1,660247;
         A[3, 3]:=A[3, 3]*1.660247;
         "PRINT"
MI IN GM/CM2*10-40
         1], A[2, 2], A[3, 3];
"IF" T[10] = 0.0 "THEN"
 , A[1,
         "BEGIN" T[12]:=T[10];
            T[10]:=T[11];
            T[11]:=T[12];
            "GOTU" UNCE
         "END";
      "END":
   "END":
"END":
```

SHAPEA can be used for x_{β} -unsaturated aldehydes and ketones. SHAPEB and SHEPEC are similar programs for x_{β} -unsaturated esters and saturated amides respectively (where these molecules can be treated as effectively planar species).

```
XLESS2:
 "BEGIN"
"COMMENT" REQUIRES PROCEDURES AKES ONand KEY;
    "REAL" SX, SXY, SXX, SY, N, C, SV, SXA, STDV,
     XX, YY, XHIGH, XLOW, YHIGH, YLOW, X1, X2, Y1,
    Y2, SCX, SCY;
"INTEGER" N, NN, I;
   "READ" NN;
     "HEGIN" "REAL" "ARRAY" X[1 : NN], Y[1 : NN], V[1 :
        NN], XA[1: NN], T[1: NN], IO[1: NN], IC[1:
        NN], IT[1 : NN], XNEW[1 : NN], YNEW[1 : NN], A[1
      : : 24];
        5X:=SXY:=SXX:=SY:=SV:=SXA:=0.0;
        "FOR" N:=1 "STEP" 1 "UNTIL" NN "DO" "IF"
        KEY(2) "THEN"
      "BLGIN" "READ" T[N], IC[N], IT[N];
           X[N] = 1.0/(T[N] + 273.0);
           Y[N]:=LN(IC[N]/IT[N])
       "END"
        "ELSE"
        "BEGIN" "READ" T[N], ID[N], IC[N], IT[N];
           X[N]:=1,0/(T[N] + 273,0);
         IC[N]:=LN(IO[N]/IC[N]);
"IF" KEY(3) "THEN" "READ" IO[N];
           IT[N]:=LN(IO[N]/IT[N]);
           Y[N]:=LN(IC[N]/IT[N]);
          \delta X := \delta X + X[N];
          SXY:=SXY + X[N]*[N];
         SXX:=SXX + X[N] * X[N]:
          SY:=SY + Y[N];
       "END":
      M:=(NN*SXY - SX*SY)/(NN*SXX - SX*SX);
      C:=(SX+SXY - SY+SXX)/(SX+SX - NN+SXX);
      "FOR" N:=1 "STEP" 1 "UNTIL" NN "DO"
       "BEGIN" V[N]:=Y[N] - M+X[N] - C;
          "IF" KEY(4) "THEN" "PRINT" V[N], Y[N], X[N];
          V[N]:=V[N]*V[N];
          SV:=SV + V[N];
          XA[N]:=X[N] - SX/NN;
          XA[N]:=XA[N]+XA[N];
          SXA:=SXA + XA[N]
       "END";
       STDV:=SQRT(SV/(SXA+(NN - 2)));
"PRINT" SAMELING, M, +OR-, STDV,
                                                 ́Ү́я`, Ж,
       X+, C;
       M:=M*1.987;
       STDV:=STDV+1.987;
       "PRINT" M. STDV;
       M:=M/1.987;
       STDV:=STDV/1.987;
       "IF" KEY(5) "THEN" "GOTO" AB;
"READ" XX, YY, XHIGH, YHIGH, XLOW, YLOW;
"EEGIN" "FUR" N:=1 "STEP" 1 "UNTIL" NN "DO"
          "BEGIN" XNEW[N]:=X[N] - XX;
             YNEW[N] := Y[N] - YY:
          "END";
```

```
X1:=XLCW;
   Y1:=M*X1 + C:
   X2:=XHIGH:
   Y2:=M*X2 + C;
   X1:=X1 - XX;
   Y1:=Y1 - YY;
   X2:=X2 - XX:
   Y2:=Y2 - YY;
   XHIGH:=XHIGH - XX;
   XLUW:=XLUW - XX;
   YHIGH:=YHIGH - YY;
   YLOW:=YLOW - YY;
   ALS AXES (XHIGH, XLAW, YHIGY, YLOW, SCX, SCY,
    1/T A', 'LN(I CIS/I TRANS)');
   "FOR" N:=1 "STEP" 1 "UNCIL" NN "DO"
   "BEGIN" MUVEPEN(XNEW[N]*SCX, YNEW[N]*SCY);
      CENCHAF (3);
   "END":
   MOVEPEN (X1*SCX, Y1*SCY);
   DRAWLINE (X2*SCX, Y2*SCY);
   I:=1:
   INSTRING(A, I);
   MIVEPEN(400, 1805);
   DRAWLINE (412, 1805);
   DRAWLINE (406, 1817);
  DRAWLINE (400, 1805);
   MOVEPEN(435, 1815);
   CENCHAR(2);
   MUVEPEN(400, 1800);
   I:=1:
   PUNCH(5);
  OUTSTRING(A, I);
MIVEPEN(500, 1505);
   DRAWLINE (512, 1505);
   DRAWLINE (506, 1517);
  DRAWLINE (500, 1505);
   MOVEPEN(535, 1515);
   CENCHAR(2);
  MUVEPEN(500, 1600);
"PRINT" PUNCH(5), SLOPE =
                                 ALIGNED(3, 1),
       +CR-, ALIGNED(2, 1), STDV;
  M:=M*1.9872;
   STDV:=STDV*1.9872;
  MOVEPEN(500, 1400);
   "PRINT" PUNCH(5),
                               , ALIGNED(3, 1),
                           -
       +OR-, ALIGNED(2, 1), STDV;
   M,
  MOVEPEN(850, 1400);
"PRINT" PUNCH(5), CALS/MOLE;
"END":
```

AB:

"END"; "END":

A SIMPLER PROGRAM ALONG SIMILAR LINES CALLED LESSER WAS ALSO USED.

1 2 .

```
DHCALC;
"BEGIN" "REAL" SX, SY, SZ, SXX, SXY, SXZ, SXXX,
  SXXY, SXXZ, A, B, C, D, E, F, AA, BB, CC,
  SXXA, SZZA, SXZA, SQ, SV, STDB,
                                       STDC:
  "INTEGER" J. N;
  "READ" N;
  "BEGIN" "REAL" "ARRAY" X[1 : N], Y[1 : N], T[1 :
     N], IO[1 : N], XA[1 : N], XXA[1 : N], ZA[1 : N],
      ZZA[1:N], XZA[1:N]_{0} V[1:N], IC[1:N], IT[1]
      : N]:
     SX:=SY:=SZ:=SXY:=SXX:=SXZ:=SXXX:=SXXY:=SXXZ:=0.0;
     SXXA:=SZZA:=SXZA:=SV:=0.0;
     "FOR" J:=1 "STEP" 1 "UNTIL" N "DO"
     "BEGIN" "READ" T[J], IU[J], IC[J], IT[J];
        X[J]:=1.0/(T[J] + 273.0);
        IC[J]:=LN(IO[J]/IC[J]);
        IT[J]:=LN(IO[J]/IT[J]);
        Y[J]:=LN(IC[J]/IT[J]);
        SX:=SX + X[J];
        SY:=SY + Y[J];
        SZ_{:=}SZ + LN(X[J]);
        SXX:=SXX + X[J]*X[J];
        SXY:=SXY + X[J]*Y[J];
        SXZ:=SXZ + X[J]+LN(X[J]);
        SXXX:=SXXX + X[J] + X[J] + X[J];
        SXXY:=SXXY + X[J]*X[J]*Y[J];
        SXXZ:=SXXZ + X[J] * X[J] * LN(X[J])
     "END":
     A:=SX - SXZ+N/SZ;
     B_{:=SXX} - SXZ + SX/SZ;
     C:=SXY - SXZ+SY/SZ;
     D:=SXX - SXXZ*N/SZ;
     E:=SXXX - SXXZ*SX/SZ;
     F:=SXXY ~ SXXZ*SY/SZ;
     BB:=(C*D - F*A)/(B*D - A*E):
     AA:=(C - B*BB)/A;
     CC:=(SY - N*AA - SX*BB)/SZ;
     "FOR" J:=1 "STEP" 1 "UNTIL" N "DO"
      "BRGIN" V[J]:=Y[J] = AA = BB*X[J] = CC*LN(X[J]);
        "PRINT" V[J], Y[J];
        V[J]:=V[J]+V[J];
        SV:=SV + V[J];
        XA[J]:=X[J] - SX/N;
        XXA[J]:=XA[J]*XA[J];
        SXXA:=SXXA + XXA[J];
        ZA[J]=LN(X[J]) - SZ/N;
        ZZA[J]:=ZA[J]*ZA[J];
        SZZA:=SZZA + ZZA[J]:
        XZA[J]:=XA[J]*ZA[J];
        SXZA:=SXZA + XZA[J]
      "END":
     SQ:=SXXA*SZZA - SXZA*SXZA:
     STDB:=SQRT(SV*SZZA/(SQ*(N - 3))):
     STDC:=SQRT(SV*SXXA/(SQ*(N - 3)));
     "PRINT" SAMELINE, AA, BB,
                                    +UR-, STDB, CC,
      +OR- STDC
  "END";
```

"END";

```
META;
"BEGIN" "INTEGER" X, Y, I;
    "REAL" Z;
"DOLLEAN" "PRIXEDURE" KEY(1);
    "VALUE" I;
   "INTEGER" I;
    "DEGIN" "CODE"
       %LDR$I
       %1D:L$1
       %SUBR:L31
       %JZ$ZERO
       %RTOK
       %SML
       $$ZERO$ST$I
       %CTOM
       %AND$I
       %ST$I
       KEY:=I "NE" O
   "END" KEY;
"INTEGER" "ARRAY" A[0 : 50];
    "PRINT" PUNCH(3),
    'IF LINE PRINTER OUTPUT REQUIRED KEY(I) DOWN ;
   WAIT;
"IF" KEY(1) "THEN" PUNCH(4) "ELSE" FUNCH(1);
    I;=0;
   N TRING(A, ...);
   I:=0;
   LUTSTRING(A, I);

"READ" X, Y, Z;

"BEGIN" "REAL" DIFF, QJ;

"INTEGER" J, K, KT, L, N, W1, W1P1, W2;

"REAL" "ARRAY" Q[1:Y];
      "INTEGER" "ARRAY" P[1 : X];
"PRINT" 12
       MODS,
       M CDS , M1 , M2 , M1-M2 , M
"FOR" J:=1 "STEL" 1 "UNTIL" X "DO" "READ"
                                                M1.-M2,
                                                            MCALC ;
       P[J]:
       "FOR" JI=1 "STEP" 1 "UNTIL" Y "DO" "READ"
       Q[J]:
       W1:=0;
LEXTP: "IF" X+(X - 1) - W1+(W1 - 1) "GE" STUREMAX - 10
       "THEN" W2:=ENTIER (SQRT (W1*(W1 - 1) + STUREMAX -
       3.75) + 0.5) "ELSE" W2:=X;
"IF" KEY(2) "THEN" "TRINT" FUNCH(3), X, W1,
       W2, STUREMAX:
       W1P1:=W1 + 1;
       "BEGIN" "REAL" "ARRAY" M[1 : (W2*(W2 - 1)"DIV"2 -
          W1*(W1 - 1)"DIV"2)]:
          "FIR" K:=W2 "STEP" - 1 "UNTIL" W1P1 "DO"
          "DEGIN" KT:=(K - 1)*(K - 2)"DIV"2 - W1*(W1 -
             1)"DIV"2;
```

```
N:=K - 1;
          "FUR" L:=N "STEP" - 1 "UNTIL" 1 "DO"
          M[KT + L]:=P[L]+P[L]/P[K]:
      "END";
      "FUK" J:=1 "STEP" 1 "UNTIL" Y "DO"
      "BEGIN" DIFF:=0.0;
          4J;=Ω[J];
          "FOR" KI=W2 "STEP"
                                 - 1 "UNTIL" W1P1 "DO"
          "DEGIN" KT:=(K - 1)*(K - 2)"DIV"2 - W1*(W1 -
             1)"DIV"2;
             N:=K - 1;
             "FOR" L: N "STEP" - 1 "UNTIL" 1 "DO"
"DEGIN" "IF" ABS (M[KT + L] - QJ) "LE" Z
                "THEN"
                "DEGIN" DIFF:=P[K] - P[L];
                   "PRINT" ALIGNED (3, 2), QJ,
PREFIX(, ), ALIGNED (3, 0),
                   F[K], P[L], DIFF, ALIGNED(3, 2),
M[(KT + L)]
                "END":
             "END";
         "END";
"IF" DIFF = C "THEN"
          "DEGIN" "PRINT" ALIGNED (3, 2), QJ,
             METASTABLE NUT ASSIGNED ;
             "IF" X "GE" 80 "THEN" "FRINT"
IN THIS DLACK
          "END"
         "ELSE" "IRINT" L
      "END";
      W1:=W2;
      "PRINT" LA":
   "END";
"IF" W2 "NE" X "THEN" "GOTO" LCOP
"END";
```

"END";

```
"PROCEDURE" ALS AXES (UX, LX, UY, LY, SCX, SCY, STRX,
STRY):
"VALUE" "JX, LX, UY, LY;
"STRING" STRX, STRY;
"REAL" UX, LX, UY, LY, SCX, SCY;
"HEGIN" "INTEGER" EX, SY, INDX, INDY, STEPS, TOTX,
   TOTY:
   "REAL" XX, YY, UNX, UNY;
"PROCEDURE" PLACE AXIS(U, L, SC, SHIFT, UNIT,
   INDEX, TOT);
"VALUE" TOT;
   "INTEGER" INDEX, TUT, SHIFT;
   "REAL" U, L, UNIT, SC;
"BEGIN" "REAL" TENN, UL, R;
      "INTEGER" I;
"IF" U < L "THEN"
      "BEGIN" R:=U:
         U:=L;
         L:=R
      "END":
      "IF" 1 > 00 "THEN" L:=0 "ELSE" "IF" U < 0
      "THEN" U:=0;
      UL_{i}=U - L_{i}
      TENN:=10 - 10;
      "FOR" I:= - 9 "STEP" 1 "UNTIL" 9 "DO"
      "BEGIN" TENN:=10.0*TENN;
         "FUR" R:=0.2, 0.3, 0.4, 0.5, 0.8, 1.0,
                                                        1.5
         "DO" "IF" UL < R*TENN*(TOT + .01) "THEN"
         "GUTO" F
      "END":
      "PRINT" PUNCH(3), "SCALE TOD GREAT":
      STUP:
F1
      SC:=STEPS/(R*TENN);
      UNIT:=k:
      INDEX:=I:
      I:=ENTIER(L/(R*TENN) + .01);
      SHIFT:= - STEPS+1:
      L:=RºI
   "END" PLACE AXIS;
   "PROCEDURE" DRAW IN(H, U, L, UNIT, INDEX, TUT,
   XX, YY);
   "VALUE" U, L, UNIT, H,
"INTEGER" INDEX, H, TUT;
                               INDEX, TUT;
   "KEAL" UNIT, U, L, XX, YY;
"BEGIN" "INTEGER" I, K, HDAR;
      "PROCEDURE" TITLE (K);
      "VALUE" K;
      "INTEGER" K;
      "BEGIN" "IF" H = 1 "THEN"
         "BEGIN" MUVEPEN(0,
                              - 200);
            "PRINT" PUNCH(5), 1 INCH ON X AXIS - ,
            ALIGNED(1, 3), UNIT, X10, DIGITS(1),
            INDEX:
            MDVEPEN(H*(K - 10) + 60, HBAR*(K + 38));
            "PRINT" PUNCH(5), STRX
         "END";
```

```
"IF" HEAR = 1 "THEN"
      "BEGIN" MOVEPEN(0, - 250);
"PRINT" PUNCH(5), 1 INCH ON Y AXIS =
         ALIGNED(1, 3), UNIT, 'X10', DIGITS(1),
         INDEX;
         MIVEPEN(H*(K - 10) + 60, HBAR*(I + 38) - 50);
         "PRINT" FUNCH(5), STRY
      "END":
      MOVEPEN(H+K, HBAR+K);
   "END":
   I:=STEPS+L/UNIT;
   HBAR:=1 - H:
   MOVEPEN(H+I, HBAR+I);
   "IF" U "LE" n = 11 "THEN" TITLE(I);
   K:=I + TUT*STEPS;
   "IF" H = 1 "THEN" LIEXX "ELSE" LIEYY;
   "FOR" II=I "STEP" STEPS "UNTIL" K "DO"
   "BEGIN" DRAWLINE (H+I, HBAR+I);
      "BEGIN" CENCHAR(1);
         MUVEPEN(H*(1 + 65) - 130, HBAR*(1 + 38) - 50);
        "PRINT" PUNCH(5), ALIGNED(2, 4), L;
      MUVEPEN(H*I, HBAR*I);
      "END";
     Lt=L + UNIT+10+INDEX;
   "END";
   "IF" U > in - 11 "THEN" TITLE(K);
"END" DRAW IN;
STEPS:=200;
           THIS IS THE NUMBER OF PLOTTER STEPS
"COLDENT"
PER UNIT : CHANGE TO SUIT PLUTTERS OTHER THAN MIDEL 4396:
WAY(0, 3);
TUTX:=5;
"COMMENT"
          WIDTH OF HIRIZONTAL ALIS IN UNITS:
CHANGE TO SUIT PURPOSE AND/LR PLOTTER:
PLACE AXIS (UX, LX, SCX, SX, UNX, INDX, TUTX);
TUTY:=8;
"COMMENT"
          LENGTH OF VERTICAL AXIS IN UNITS:
CHANGE TO SJIT PURPOSE AND/OR PLOTTER;
PLACE AXIS (UY, LY, SCY, SY, UNY, INDY, TUTY);
"COMMENT" THE FULLOWING CODE MERELY PRODUCES THE VERTICAL
SHIFT SY WITHOUT REQUIRING A SECOND TIMEWASTING CALL OF SETORIGIN;
"CODE"
% LD:L $ 1
%UCUM $ 6
% JS:L $ 4
% LD:L $ 16
% LIDUM S 6
% JS:L S 4
% LD:L $200
%ADDS $ SY
% LD:L $ 4
%DECS $ SY
% JN S LL
% CDUM S 6
% JS:L $ 4
% JS:L $10
$$ IL $ IDK:L $ 0;
SETURIGIN(SX + 295, 0);
```

MOVEPEN(O, O); "PRINT" PUNCH(3), CENTRE PEN ON NEAREST GRID'; WAIT; DRAW IN(1, UX, LX, UNX, INDX, TOTX, XX, YY); DRAW IN(O, UY, LY, UNY; INDY, TUTY, XX, YY); "END" ALS AXES:

THIS PROCEDURE (ALS AXES) IS BASED ON A SIMILAR PROCEDURE CALLED AXES ON WRITTEN BY THE COMPUTER UNIT STAFF AT KINGSTON. AXES ON IS USED IN SHAPFA, BUT BECAUSE OF ITS LENGTH AND SIMILARITY TO ALS AXES, IT IS NOT SHOWN HERE.

DLINE IS A PROCEDURE (PROVIDED BY THE COMPUTER UNIT STAFF) USED IN SHAPEA;

"PROCEDURE" DLINE (X1, Y1, X2, Y2); "VALUE" X1, Y1, X2, Y2; "REAL" X1, Y1; "INTLGER" X2,Y2; "DEGIN" "REAL" XR, YR, L; "INTEGER" I,S; XR:=X2-X1; YR:=Y2-Y1; L:=SURT(XI(*XI(+YR*YR); S:=1/10+0.5; "IF" S"DIV"2+2=S "THEN" S:=5+1: XR:=XR/S; YR:=YK/S; S:=(S-1)/2; MINEPEN(X1,Y1); "FUR" I:=1 "STEP" 1 "UNTIL" 5 "DO" "DEGIN" X1;=X1+XR; Y1:=Y1+YR; DRAWLINE (X1, Y1); X1:=X1+XR; Y1:=Y1+YR; MINEPEN(X1,Y1) "END": DRAWLINE (X2, Y2);

MANEPEN(X2,Y2) "END" OF PROCEDURE DLINE:

Statistical Analysis of Results

Least squares analysis of straight line.

It is common to be presented with a set of values of a function (Y) which may be linearly dependent on values of a known parameter (X). This can be represented by the equation

Y = a + bX

For many types of studies, the values of a and b are important. Their values with standard deviations are required either as important figures in themselves or to obtain unknown values of X from known Y or vice versa. E.g. from the expression

 $\Lambda = \mathcal{E}cl + K$

where 1 is fixed, calculation could be made of A from c, c from A, \mathcal{E} from the slope.

Because the values of Y which are experimentally obtained contain errors of measurement, no single values of a and b can be chosen to satisfy a series of n sets of values of X and Y. Parameters are chosen which would best satisfy all the equations. A criterion for "best fit" must be decided upon. This criterion is often that of the "least squares" treatment but many other criteria could be chosen which could produce somewhat different answers.

Values of a and b are chosen such that the sum of the deviations of $(Y \text{ obs } - Y \text{ calc})^2$ is a minimum

 $\begin{aligned} & \left(Y_{obs} - Y_{calc} \right)^{2} = \text{minimum} \\ & \frac{d}{da} \xi \left(Y \text{ obs} - Y \text{ calc} \right)^{2} = 0 \\ & \frac{d}{db} \xi \left(Y \text{ obs} - Y \text{ calc} \right)^{2} = 0 \end{aligned}$

Thus

 $\frac{d}{da} \left(\sum (y - a - bx)^2 \right) = \mathbf{0}$ $\frac{d}{db} \left(\sum (y - a - bx)^2 \right) = 0$ $-2 \sum (y - a - bx) = 0$ $\sum x \left(\sum y - a - bx \right) = 0$ $\sum y - \sum a - b \sum x = 0$ $\sum y - \sum a - b \sum x = 0$ $\sum x y - \sum a - b \sum x^2 = \mathbf{0}$ $\sum a = na$ $na + b \sum x = \sum y$ $a \sum x + b \sum x^2 = \sum xy$

Thus

$$a \leq x + b \leq x^{2} = \leq xy$$
Thus a (intercept)
$$\frac{\leq y \leq x^{2} - \leq x \leq xy}{n \leq x^{2} - (\leq x)^{2}}$$

$$b \text{ (slope)} = \frac{n \leq xy - \leq x \leq xy}{n \leq x^{2} - (\leq x)^{2}}$$

a, b often called regression coefficients. Variance of Y is given by

$$s_y^2 = \frac{\sum (Y \text{ obs } - Y \text{ calc})^2}{n - 2}$$

N.B. n-2; two degrees of freedom are used to determine the parameters of the straight line.

Variance of a is given by

$$s^{2} = \frac{s^{2} \leq x^{2}}{n \leq x^{2} - (\leq x)^{2}}$$

Variance of b by

$$s_{b}^{2} = s_{y}^{2} n$$

 $n \overline{\xi x^{2} - (\xi x)^{2}}$

or dividing by n



Similar calculations can be made for the treatment of the quaffratic

 $y = a+bx+cx^2$

APPENDIX III

Short courses attended during the period 1966 - 1969 while pursuing research for a higher degree.

1966 - 1967

Nuclear Magnetic Resonance Spectroscopy (6 lectures) Application of Group Theory to Chemical Problems (6 lectures) Molecular Structure Methods (Practical) (10 sessions) Introduction to Algol Programming (6 lectures)

1967 - 1968

Applications of Mass Spectrometry (6 lectures) Interpretation of N.M.R. Spectra (6 lectures) Spectroscopic Methods of Trace Analysis (6 lectures) The Chemistry of Drugs (6 lectures) Ninth European Congress on Molecular Spectroscopy (Madrid) (1 week)

1968 - 1969

The Role of Patents in the Chemical Industry (6 lectures) The following sections of the M.Sc. in Molecular Spectroscopy at Kingston:-Group Theory (3 lectures) Microwave Spectroscopy (3 lectures) Vibrational Spectroscopy (12 lectures) Wave Mechanics and Electronic Spectroscopy (10 lectures) Spectroscopic Methods in Organometallic Chemistry (2 days) (Symposium at Kingston) Various 1 day meetings including I.R.D.G. meetings. College Research Colloquia given by internal and external lecturers on research or topics of general interest.