

INFRARED SPECTRAL ANALYSES OF THE  
CONFORMATIONAL BEHAVIOUR OF CERTAIN  
1,2-DISUBSTITUTED ETHANES



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by

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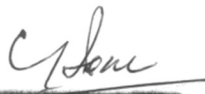
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C E R T I F I C A T E

Certified that the work incorporated in the thesis "Infrared Spectral Analyses of the Conformational Behaviour of certain 1,2-disubstituted Ethanes" by Shri V. KRISHNAN was carried out by the candidate under my supervision. Such material, as has been obtained from other sources, has been duly acknowledged in the thesis.



Dr. C. I. Jose  
Supervisor

A C K N O W L E D G E M E N T

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(V. Krishnan)

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CHAPTER - I

INTRODUCTION

I :        A : ROTATIONAL ISOMERISM

The concept of rotation around a bond is fundamental to the structure of molecules and an understanding of this bond property was sought during the forties of this century. The formation of well defined cis, trans-isomers in the case of double bonded compounds was already known, but the absence of such isomeric species in the case of the single bonded compounds was assumed to be due to 'free rotation'.

The experimental methods that yielded new information on this question were dipole moment measurements, vibrational spectroscopic analysis and electron diffraction patterns. The dipole moment measurements of many symmetrical haloethanes in solution had given values between those calculated for a trans structure which would be nearly zero and those of a gauche conformer having a relatively high value and showed a temperature dependence for the dipole moment. The vibrational analysis by infrared and Raman spectroscopic techniques revealed considerable differences in the spectra of these haloethanes in the various physical states. Thus vibrational spectra in the liquid and gaseous states were more complex and having additional bands over those in the solid state suggesting additional species in the latter states over those in the solid state. Similarly, electron diffraction patterns of these haloethanes in the vapour could be explained only by postulating the presence of both

the trans and gauche species in the vapour.

The above results could be rationalised to conclude that rotation around a single bond is not free and there is more than one potential minimum during a single rotation. Alternatively, there could be a broad single potential minimum about which two movable groups exert torsional vibrations of large amplitude.

Ethane was one of the first to be considered for the study of internal rotation around a single bond. The potential curve could be obtained theoretically if we know the interaction of the hydrogen atoms of one methyl group with those of the other which prevents free rotation about the C-C axis. Assuming a single type of interaction energy Eyring calculated the height of the potential barrier to internal rotation in ethane as 0.3 Kcal/mol as against the observed value of 2.75 Kcal/mol.

I :        B : 1,2-DICHLORO- and DIBROMOETHANES

Mizushima et al<sup>1</sup> were the first to investigate the conformational equilibria of 1,2-dihaloethanes in detail using spectroscopic methods. Their Raman spectral studies of solid and liquid 1,2-dibromo and 1,2-dichloroethanes revealed distinct additional bands in the liquid over those in the solid state suggesting the presence of more than one species in the former. Additional infrared bands in the gaseous state compared

to the solid also pointed to the occurrence of more than one species in the former. These results were interpreted to indicate that the both dichloro and dibromo ethanes contained trans isomeric species in the solid state and both the trans and gauche species in the liquid and gaseous states. As an extension, Wada's results<sup>1</sup> in solution showed the presence of a mixture of isomeric whose relative proportion depended on the dielectric constant of the solvent. These spectroscopic results found support in dipole moment, electron diffraction and x-ray diffraction studies of these molecules. While a complete trans structure was found to be present in solid dichloroethane by x-ray analysis<sup>2</sup>, the electron diffraction study<sup>3</sup> of the vapour of 14°C showed nearly 80% trans and 20% gauche species. Dipole moment measurements<sup>4</sup> of 1,2-dichloroethane in the gaseous state (boiling point) indicated the presence of nearly 75% trans and 25% gauche species, while for the liquid, it was about 56% gauche and 44% trans<sup>5</sup>. The energy difference<sup>4</sup> between the two rotational isomers were found to be 1.22 Kcal/mole and 1.4 Kcal/mole for gaseous 1,2-dichloro and dibromoethanes respectively. The larger difference in the case of bromo derivative was explained on the higher steric repulsion between the bromine atoms.

Tanabe<sup>6</sup> made a detailed study of the infrared bands of liquid and gaseous 1,2-dichloro and 1,2-dibromo ethanes. He determined the intensities of the various bands and showed that they agreed with the calculated intensities based on the interchangeability of intensity parameters between trans and gauche species. The role of the dielectric

constants<sup>7</sup> of the solvent in determining the relative population of trans, gauche species in solution has been investigated by measuring the relative intensities of C-X bands corresponding to the two species. The polar gauche conformer is more favoured in high dielectric constant solvent.

I : C : 1,2-DIAMINOETHANE

In 1,2-diamino ethanes, the early spectroscopic studies however did not yield clear cut conclusions regarding the nature of the species in the various states as in 1,2-dihalo ethanes. Bellanato<sup>8</sup> who had studied the Raman and infrared spectra of ethylene diamine concluded that it exists mainly as a cis isomer in the liquid state. Since ethylene diamine has been found to exist mainly as gauche and in some cases even in the trans form in many of its metal complexes, Sabatini and Califano<sup>9</sup> made an exhaustive study of the Raman and infrared spectra of ethylene diamine and its N-deuterated derivatives in the solid, liquid and gaseous states. They concluded that there is essentially only one conformer in all the three states which is most probably cis, but may be gauche as there are arguments to favour one or the other. However, the trans form was ruled out. Kimura et al<sup>10</sup> who measured the dipole moments of ethylene diamine and its oligomers in benzene found that the observed dipole moments agreed with the values calculated on the basis of cis/gauche structure for ethylene diamine and concluded from lack of temperature dependence that intramolecular hydrogen bonding is absent or weak.

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Krueger who had extensively investigated a series of mono, di and tri amines and their N-alkyl derivatives had concluded from the asymmetric and symmetric NH stretching frequencies and their relative intensities that there are intramolecularly hydrogen bonded gauche species of ethylene diamine in tetrachloroethylene solution.

The electron diffraction studies<sup>12</sup> of ethylene diamine in the gas phase at 50-120°C revealed mainly gauche conformation with contributions from other conformations not exceeding 5%.

X-ray crystallographic studies<sup>13</sup> of ethylene diamine at -60°C however showed that the molecule takes a trans conformation in the solid with a planar N-C-C-N skeleton and N-H...N intermolecular hydrogen bonds.

Solution spectra<sup>14</sup> of ethylene diamine, its c-deuterated, N-deuterated and per deuterated analogues in carbon tetrachloride and cyclohexane established that the gauche conformation (C2 symmetry) predominated in solution. Assignments of the various vibrational modes could be carried out satisfactorily on this basis.

Aqueous solution<sup>15</sup> spectra of ethylene diamine however showed that while it existed as trans species its acid salt acquired a gauche conformation in water.

Infrared and Raman spectral studies of ethylene diamine at 200 K (close to the temperature at which X-ray crystallographic studies<sup>13</sup> were earlier performed) and 70 K were carried out to establish the nature of the species at low

temperatures<sup>16</sup>. It was found that the trans species found by X-ray crystallographic studies at 200 K underwent a phase transition near 78 K in which the N-C-C-N skeleton remained intact (trans), but due to rotation of the C-N bonds the NH<sub>2</sub> groups became gauche to the CH<sub>2</sub> groups compared to the trans conformations above 78 K.

Recent microwave studies<sup>17</sup> revealed that two gauche conformations having intramolecular hydrogen bonding predominated with little probability of other conformations being present to any appreciable extent.

Y. Omura and T. Shimanouchi<sup>18</sup> studied the conformation of ethylene diamine in liquid, vapour and cyclohexane solution using Raman spectra below 700 cm<sup>-1</sup>. In liquid it was found to be a mixture of trans and gauche species whereas in gaseous and solution phases it existed only in the gauche form.

I : D : 1,2-DIHYDROXYETHANE

Conformational behaviour of ethylene glycol in the various physical states has been studied by many workers. Bastiansen<sup>19</sup> who first studied the electron diffraction pattern of ethylene glycol concluded the absence of any trans species in its vapour. Raman spectral analysis<sup>20</sup> of ethylene glycol vapour showed the presence of cyclic intramolecularly hydrogen bonded species absorbing at 3660 cm<sup>-1</sup> which on heating went over to free species absorbing at 3692 cm<sup>-1</sup>.

Krishnan and Krishnan<sup>21</sup> concluded from the infrared spectral analysis of liquid and solid ethylene glycol that it is gauche in the solid state while both gauche and trans forms are present in the liquid. In aqueous solution the gauche species were exclusively found. Buckley and Giguere<sup>22</sup> and Matsuura and Miyazawa<sup>23</sup> on the other hand concluded from infrared and Raman spectra that it exists in the gauche form in the solid, liquid and gaseous states. The gauche conformation in the liquid state found support in the infrared and Raman spectral analysis of ethylene glycol by Sawodny et al.<sup>24</sup>.

Laser Raman spectral analysis of ethylene glycol in the temperature range 20-100°C by Matsuura et al.,<sup>25</sup> however, showed that both trans and gauche species are present in the liquid state. The intensity changes of the trans and gauche Raman lines at 481 and 523  $\text{cm}^{-1}$  provided a value of 0.7 Kcal/mol for the energy difference between the two species.

Krueger and Mettee<sup>26</sup> were the first to investigate conformational behaviour in dilute solution. The appearance of a new band at 3614  $\text{cm}^{-1}$  at low temperatures in addition to the bands at 3644 and 3604  $\text{cm}^{-1}$  and the temperature dependence of their peak absorbances led them to postulate the formation of bicyclic intramolecular hydrogen bonded species with two O-H...O bonds in addition to the intramolecularly hydrogen bonded five membered ring species.

Busfield et al.<sup>27</sup> recently studied the dilute solution spectra of glycols  $\text{OH}-(\text{CH}_2)_n-\text{OH}$   $n = 2-6$ . From an analysis of



the hydroxyl stretching bands in the temperature range 20-70°C they obtained an enthalpy value of 5.3 Kcal/mol for the conversion of the five membered intramolecularly hydrogen bonded species to free species assuming the extinction coefficients of two hydroxyl bands to be the same. Recently, infrared spectra<sup>28</sup> of ethylene glycol were reported in Argon matrix. Two intramolecularly hydrogen bonded species were found as expected from the abinitio calculations to be the most stable; the spectra were however complicated by matrix splitting and infrared radiation effects.

I : E : METHYLENE STRETCHING INTENSITY

The methyl and methylene stretching band intensities have been found to have a constant value per unit group in a large number of straight chain hydrocarbons, so that they ~~may~~ have been used to determine their number in such systems. If the immediate environment of the CH<sub>3</sub>, CH<sub>2</sub> groups was however changed particularly with attachment of an electronegative group adjacent to it, a marked decrease in the intensity of their stretching mode was noticed<sup>29</sup>. Early observations were made on compounds containing hydroxy, methoxy and oxymethylene groups. Barrow<sup>30</sup> showed that the intensity of the carbonyl groups varies markedly with the type of substituent adjacent to the carbonyl. A comparison of the absolute intensities of the CH<sub>3</sub> stretching modes of acetone vapour<sup>31</sup> and hydrocarbons showed that the unit intensities of the CH<sub>3</sub> group in the former was smaller than in the latter by a factor of four. Integrated absorption intensities of the methyl groups in various chloromethyl silanes<sup>32</sup> were found to decrease with increasing chlorine substitution from 570 in [CH<sub>3</sub>]<sub>4</sub>Si to 25 in CH<sub>3</sub>SiCl<sub>3</sub>. The

methyl intensity in the halomethanes also showed marked reduction compared to the intensity in methane. Higuchi et al.<sup>33</sup> also found the fall in intensities of  $\text{CH}_3$  symmetric vibration in compounds  $\text{CH}_3\text{X}$  where X is an electronegative group and tried to relate the change to Taft  $\sigma$  factors.

In the present work, the conformational behaviour of 1,2-dichloro, dibromo, diamino and dihydroxy ethanes has been studied in liquids and dilute carbontetrachloride solution to determine the relative amounts of trans and gauche species. The influence of the halo, amino and hydroxyl substituents on the integrated absorption intensity of the  $\text{CH}_2$  stretching modes has also been examined to understand the nature of the electronegative substituent on the intensity parameter.

CHAPTER - II

VIBRATIONAL SPECTROSCOPY

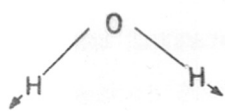
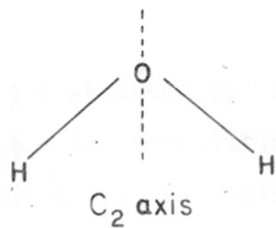
II :     A : THEORY

Vibrational spectroscopy is used extensively to determine molecular structure of simple molecules<sup>34</sup>. If there are  $n$  atoms in a molecule, the number of vibrational modes is given by  $(3n-6)$ , or  $(3n-5)$  in the case of linear molecule, the translational and rotational motions being accounted for by 3(or 2) coordinates respectively. The vibrational frequencies are largely determined by the force constants acting between the atoms and their masses.

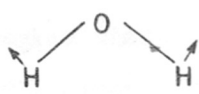
In the case of simple diatomic molecule, it is evident that it can have only one ( $n = 2, 6-5 = 1$ ) fundamental vibration. In the linear triatomic molecule water, there are 3 allowed vibrational modes and they may be represented as shown in the Fig. along side where the arrows attached to each atom show the direction of its motion during one half of a vibration. The motions 1, 2 and 3 are described as symmetric stretching, symmetric bending and antisymmetric stretching vibrations depending on the nature of the change in molecular shape. These three vibrational motions are also referred to as the normal modes of vibration (or normal vibrations) of the molecule; in general a normal vibration is defined as a molecular motion in which all the atoms move in phase and with the same frequency.

II :     B : INFRARED AND RAMAN SPECTRA

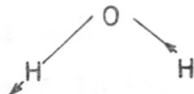
Vibrational spectra can be studied as absorption spectra of the direct transitions in the infrared region of the electromagnetic radiation or as Raman shifts in the



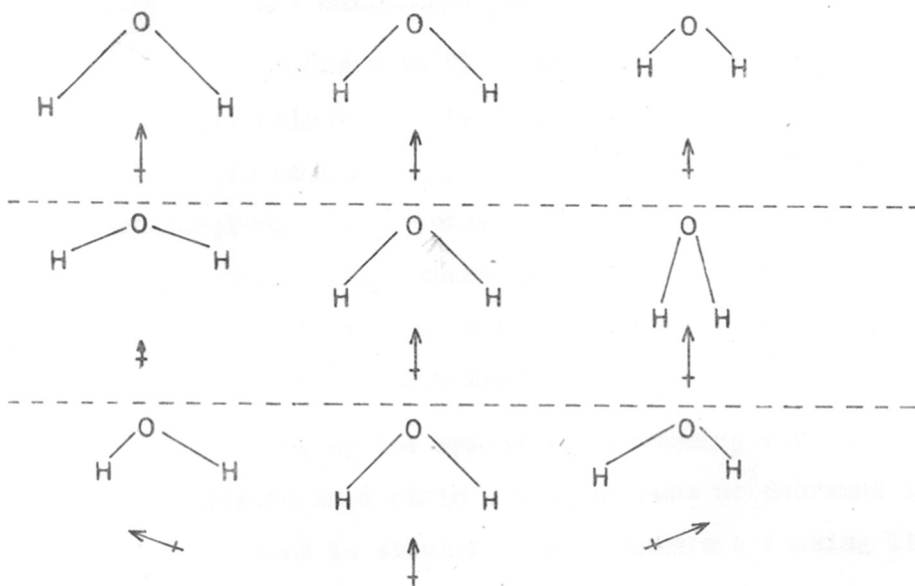
1



2



3



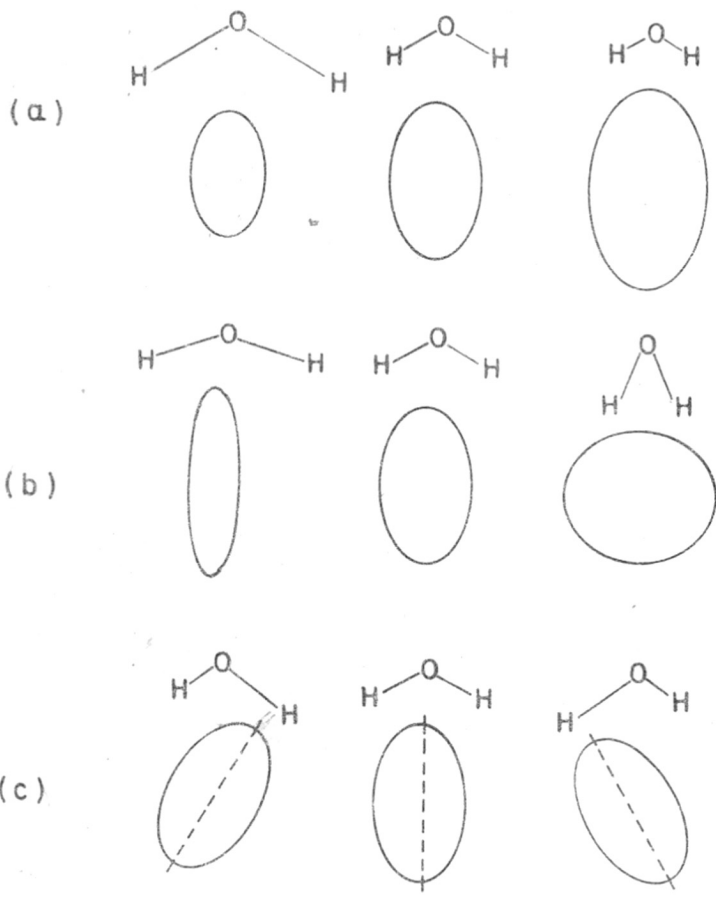
ELECTRIC DIPOLE MOMENT VARIATION IN WATER MOLECULE

scattered light obtained by irradiation with ultraviolet or visible light. The transitional probability (or activity) which determines the intensity of a band is dependent on the nature of a given vibration. For a vibration to be active in the infrared region there should be change in the dipole moment during the given vibration. In the Raman spectra, the activity is based on a change in polarisability during the vibration.

II :      C : WATER MOLECULE

In order to find out whether any or all of the three vibrations of water are infrared active, the nature of the dipole moment change during the three vibrations has to be analysed. It is evident from the vibrations below that in all three cases, there is change in dipole moment during the vibration so that these three vibrations would give rise to infrared absorption bands.

During the symmetric stretching vibration (a) bonds in the molecule as a whole would increase or decrease in length. When the bond is stretched, the electrons forming it are less firmly held by the nuclei and so the bond becomes more polarisable. Thus the polarisability ellipsoid of  $H_2O$  may be expected to decrease in size while the bonds stretch, and to increase while they compress, but to maintain an approximately constant shape. For the bending motion (b) at one extreme the molecule approaches linear configuration with a horizontal axis while at the other extreme it approaches a diatomic molecule with a vertical axis. In the asymmetric stretching motion (c), the direction of the major axis changes markedly.



POLARIZABILITY ELLIPSOID FOR THE THREE VIBRATIONAL MODES OF WATER

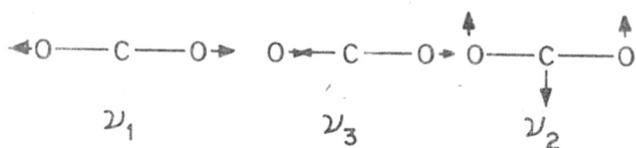
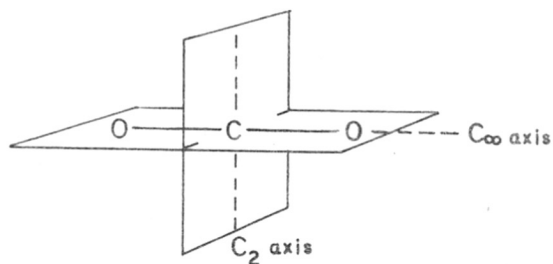
Thus in all three vibrations, polarisability ellipsoid show marked changes and therefore are all Raman active.

II : D : CARBON DIOXIDE MOLECULE

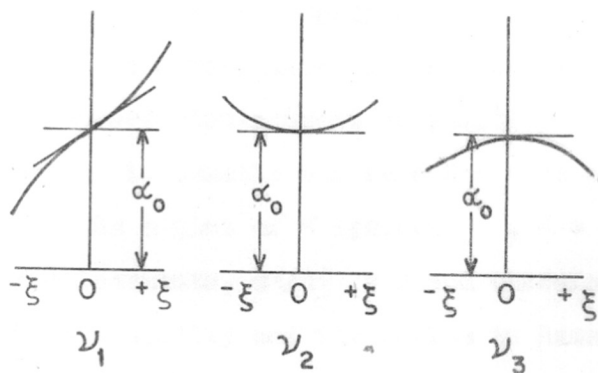
For a linear triatomic molecule like carbon dioxide (3 x 3-5) the four vibrational modes would have to be considered. The possible motions of the atoms in the molecule (depicted along side) shows that the symmetric bending mode could take place when the two oxygens move in the plane of the paper as shown or in and out of this plane. The two motions are identical in all respects except direction and are termed degenerate vibrations. The symmetric and antisymmetric stretching motions would represent the remaining two vibrational modes of the carbon dioxide molecules. If the nature of these vibrations are examined, it is evident that during the symmetric stretch, no change in dipole moment is involved, while in the other modes, a change in the dipole moment takes place. Thus in carbon dioxide molecule, the symmetric stretching mode alone would remain inactive in the infrared region.

In order to determine their Raman activity, the extreme and equilibrium configurations of the molecule and their approximate polarizabilities ellipsoids will have to be considered. Since the change of molecular shape during the vibrations may not always determine the change in the polarizability ellipsoid, it is important to take into account the change of polarizability with some displacement coordinate ( $\xi$ ) as shown in the figure along side. Thus for a





VIBRATIONS OF CARBON DIOXIDE MOLECULE



VARIATIONS OF POLARIZABILITY  $\alpha$  WITH DISPLACEMENT COORDINATE  $\xi$  DURING THREE VIBRATIONS IN CARBON-DIOXIDE

stretching motion,  $\xi$  is a measure of the extension ( $+\xi$ ) or compression ( $-\xi$ ) of the bond under consideration. For the bending mode an increase or decrease from the equilibrium bond angle would be considered positive or negative  $\xi$  respectively.

For the infrared inactive  $\nu_1$  stretch of carbon dioxide, if equilibrium value of the polarizability is  $\alpha_0$  then when the bonds stretch ( $+\xi$ ),  $\alpha$  increases and when the bonds contract ( $-\xi$ )  $\alpha$  decreases. Thus near the equilibrium position, there is a distinct change in  $\alpha$  with change in i.e.  $d\alpha/d\xi \neq 0$  at  $\xi = 0$ . Thus, for small displacements, the motion produces a change in polarizability and is therefore Raman active.

For the bending  $\nu_2$  vibration, if we count the downward displacement of the oxygen atoms as negative  $\xi$  and an upward displacement as positive  $\xi$ , it is clear that the change is exactly the same for both positive and negative  $\xi$ . Thus in a plot of  $\alpha$  against  $\xi$ ,  $\alpha = \alpha_0$  at  $\xi = 0$ . For small displacements,  $d\alpha/d\xi = 0$  and therefore no change in the polarisability and the motion is Raman inactive.

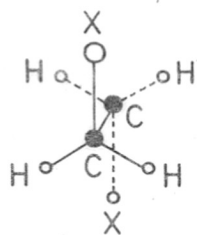
For the asymmetric stretching mode  $\nu_3$ , the polarizability decreases equally for positive and negative  $\xi$ , so that  $d\alpha/d\xi = 0$  for small displacements and the motion is Raman inactive. Thus we see that for carbon dioxide molecule only one vibration i.e. the symmetric stretch which is infrared inactive is allowed in the Raman spectrum. Further we arrive

at the important rule of mutual exclusion according to which a molecule having a centre of symmetry, Raman active vibrations are infrared inactive and Raman inactive vibrations are infrared active. If there is no centre of symmetry then some (but not necessarily all vibrations) may be both Raman and infrared active. The converse of this rule is also true i.e. the observance of Raman and infrared spectra showing no common vibrations implies that the molecule has a centre of symmetry, except sometimes that a vibration may be Raman active but too weak to be observed. However, if some vibrations are observed to give coincident Raman and infrared absorptions, it is certain that the molecule has no centre of symmetry. Thus, valuable structural information can be obtained by comparing infrared and Raman spectra.

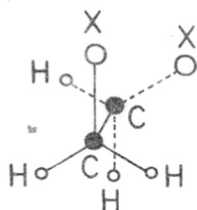
II : E : 1,2-DISUBSTITUTED ETHANES

In the case of symmetrically substituted 1,2-ethanes, there is a centre of symmetry for the trans configuration which is among the three possible configurations including gauche and cis species for this molecule. The cis species with eclipsed chlorine atoms would be an unlikely configuration from point of view of steric factors and was therefore omitted from further consideration.

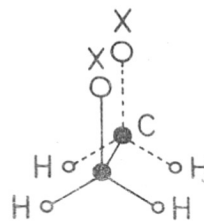
If vibrations that are symmetric or antisymmetric to a centre of symmetry are designated by the subscript 'g' and 'u' and if 'A' and 'B' are non-degenerate types symmetric and antisymmetric to rotation about the Z axis, then the  $(24-6)=14$



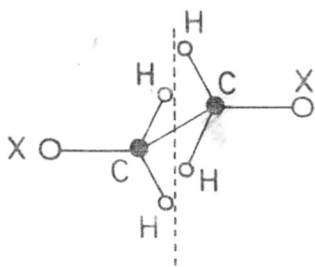
trans



gauche



cis



$C_{2h}$



$C_2$

CONFIGURATIONS OF 1,2 DISUBSTITUTED ETHANE

vibrational modes can be classified if we realise the point groups of the trans and gauche species. For the simple 1,2-haloderivatives the point group of the trans form is  $C_{2h}$  which contains a reflection in a horizontal plane passing through the C-C axis and two halogen atoms and rotation through an angle of  $180^\circ$  about the Z axis perpendicular to the C-C axis. The point group for the gauche form is  $C_2$  which contains a rotation through  $180^\circ$  about the Z-axis.

On this basis, the observed Raman and infrared frequencies should satisfy the following activity conditions. The Raman active  $A_g$  and  $B_g$  modes of the trans species should be infrared inactive and the Raman inactive  $A_u$  and  $B_u$  modes should be infrared active. For the gauche species A and B modes should be active both in Raman effect and infrared spectra.

These conclusions were indeed found to be true for the 1,2-dichloroethane which showed distinctly different infrared and Raman frequencies in the solid state and additional frequencies which were comparable in the liquid and gaseous states. The presence of only trans species in the solid and a mixture of both trans and gauche species in liquid and gaseous states were confirmed from X-ray crystallographic and dipole moment measurements.

CHAPTER - III

EXPERIMENTAL METHODS

III : A : PREPARATION

The four compounds 1,2-dichloro ethane (Riedel), 1,2-dibromo ethane (E. Merck), ethylene diamine (Riedel) and ethylene glycol (E. Merck) used in the present study were chemically pure grade materials, which were further purified by distillation and dried over molecular sieves (Linde 4A). In the case of ethylene diamine drying over sodium was necessary to remove water completely. The carbon tetrachloride and carbon disulphide used for solution studies were Analar grade and dried over molecular sieves.

III : B : INSTRUMENTAL

The spectra were recorded on SP3-300 Pye Unicam and Perkin-Elmer 221 Infrared spectrophotometers. The latter was equipped with sodium chloride prism grating interchange. The instruments were calibrated with carbon dioxide and water vapour bands and the calibration was checked with polystyrene bands before recording each spectrum. An expansion scale (4 or 5) was used when band intensities were required to be measured. The vapour phase spectra were recorded using Perkin-Elmer 10 cm or 1 meter path length gas <sup>cells</sup>. The liquid spectra were recorded with a 0.1 mm path length cell. The solution spectra were taken with a variable path length cell manufactured by Perkin-Elmer (path length 0-0.6 cm) or constructed locally in the National Chemical Laboratory Workshop (path length 3-4 cm). Path lengths were calibrated using interference fringes. Solutions were usually made by weighing the sample in a volumetric flask and making up the volume with solvent.

The following instrumental parameters were maintained for recording routine spectra. For PYE UNICAM, I.R. spectrophotometer Ratio recording mode - auto smooth, scan time 7 minutes, response 2 (fast), expansion scale 5 and spectra set ON. For PERKIN-ELMER IR spectrophotometer, slit programme 960, attenuator speed 1100, amplifier gain 2.5, suppression 4 and expansion scale 4.

### III : C : INTENSITY MEASUREMENTS

The observed absorbance values are good measure of the intensity if the bands are free from overlapping and absorbance values are in the range 0.2-0.8. Therefore, the absorbances were used to determine the individual band intensities of gauche and trans species and their relative populations with the assumption that the individual intensity parameters are interchangeable between the two species. However, for determining the total intensity of the  $\text{CH}_2$  stretching modes of the four substituted ethanols, the area of the total band was measured by graphical integration.

The integrated absorption intensity B is given by

$$B = \frac{1}{c\ell} \int \ln \left( \frac{I_0}{I} \right)_{\nu} d\nu$$

where  $I_0$  and  $I$  are the transmittances of the incident and transmitted radiation at the spectrometer frequency  $\nu$ . The concentration  $C$  and path length  $\ell$  are expressed in mole/dm<sup>3</sup> and cm respectively. For a given band, the total band area was determined by measuring transmittances at intervals of

2.5 cm<sup>-1</sup> and adding them up for the whole band.  
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CHAPTER - IV

1,2-DIHALOETHANES

IV :            A : RESULTS AND DISCUSSION

Infrared spectra of 1,2-dichloro and dibromo ethanes in the C-H and C-halogen stretching regions are shown in Figs. 1-4 for the liquid, solution and vapour states obtained at 30°C (room temperature) and the bands are tabulated in tables 1 and 2. Based on the assignments of Tanabe<sup>6</sup> who found that the intensities of the trans and gauche bands are interchangeable in dihalo ethanes, absorbances of the bands ascribable to the trans and gauche species along with the trans/gauche ratios taking into account the degeneracy of the modes are also given in the table. Absorbances were read directly from the expanded scale spectra in all cases including those of the overlapping bands where errors from such a procedure could be generally as much as 25%.

IV :            B : 1,2-DICHLORO ETHANE

In 1,2-dichloro ethane the bands obtained by us are in good agreement with those found by Tanabe. The trans/gauche ratio as determined from band absorbances in the CH<sub>2</sub> and C-Cl stretching regions were 1.8 and 2.4 respectively. In solutions of 1,2-dichloro ethane, two solvents were used to determine the trans/gauche ratios. In the CH<sub>2</sub> stretching region, the trans/gauche ratio in carbon tetrachloride was 2.7 as against 5.5<sup>obtained</sup> in the C-Cl stretching region in carbon disulphide. In the vapour state as can be seen there was considerable overlapping of bands in the CH<sub>2</sub> stretching region and therefore the absorbances measured for the trans and gauche bands could be in error by at least 3-4 times than in the usual measurements.

Thus while a value of 18 was obtained from C-Cl stretching modes, the trans/gauche ratio obtained from the CH<sub>2</sub> stretching bands was 6.5.

Mizushima<sup>1</sup> had reported Wada's results on the trans/gauche population of 1,2-dichloro ethane in the liquid and solution states from C-Cl stretching modes. While a value of 1.4 was reported for the neat liquid, for solution in hexane a value of 5 was reported. Elbermani et al<sup>7</sup> had reported trans/gauche ratios for ethylenedichloride in the liquid, in CS<sub>2</sub> solution and vapour states which were 3.0, 7.2 and 13.4 respectively which are in better agreement with our values than those of Wada's. Tanabe<sup>6</sup> reported trans/gauche ratios of 1,2-dichloro ethane and dibromo ethane in the liquid and vapour states obtained from a calculation of the intensities of the various bands in their infrared spectra. These values 0.54 and 3.3 for the liquid and the vapour spectra are much lower than the present values. The present results thus show that 1,2-dichloro ethane exists predominantly as a trans conformer in the three states. While the trans species is twice as much as the gauche in the liquid, its proportion increases to nearly four times that of the gauche in solution and more than 10 times in the vapour state. X-ray diffraction studies had found that it exists entirely in the trans form in the solid state.

IV :        C : 1,2-DIBROMO ETHANE

In the 1,2-dibromo ethane, the bands in the CH<sub>2</sub> and C-Br stretching regions are in agreement with those found by Tanabe<sup>6</sup>. In the liquid state the ratio of trans/gauche

was found to be 3.3 from the absorbances in the  $\text{CH}_2$  stretching region as compared to a value of 4.2 obtained from the C-Br stretching modes. In solution the value of 3.5 obtained for trans/gauche ratio from the  $\text{CH}_2$  stretching modes is much smaller than the value of 12.2 obtained from the C-Br stretching modes. The ratios in the vapour state from the  $\text{CH}_2$  and C-Br stretching modes were 7.0 and 11.6 respectively.

Mizushima<sup>1</sup> reported Wada's results for 1,2-dibromo ethane for the trans gauche ratios from C-Br stretching modes in the liquid and solution states. A value of 11 was reported for the ratio in the pure liquid and a value of 15 for solutions in hexane. Elbermani et al<sup>7</sup> however reported values of 2.5 and 3.8 for the liquid and solution in carbon disulphide from measurements of C-Br stretching mode intensities. Though the agreement among the various values is not good the trend is quite evident. Thus as in the 1,2-dichloro ethane, the trans species predominate and continuously increase in going from the pure liquid to solution and eventually to the vapour state. Thus from 75-80% in the liquid the amount of trans species increases to nearly 90% in the vapour state.

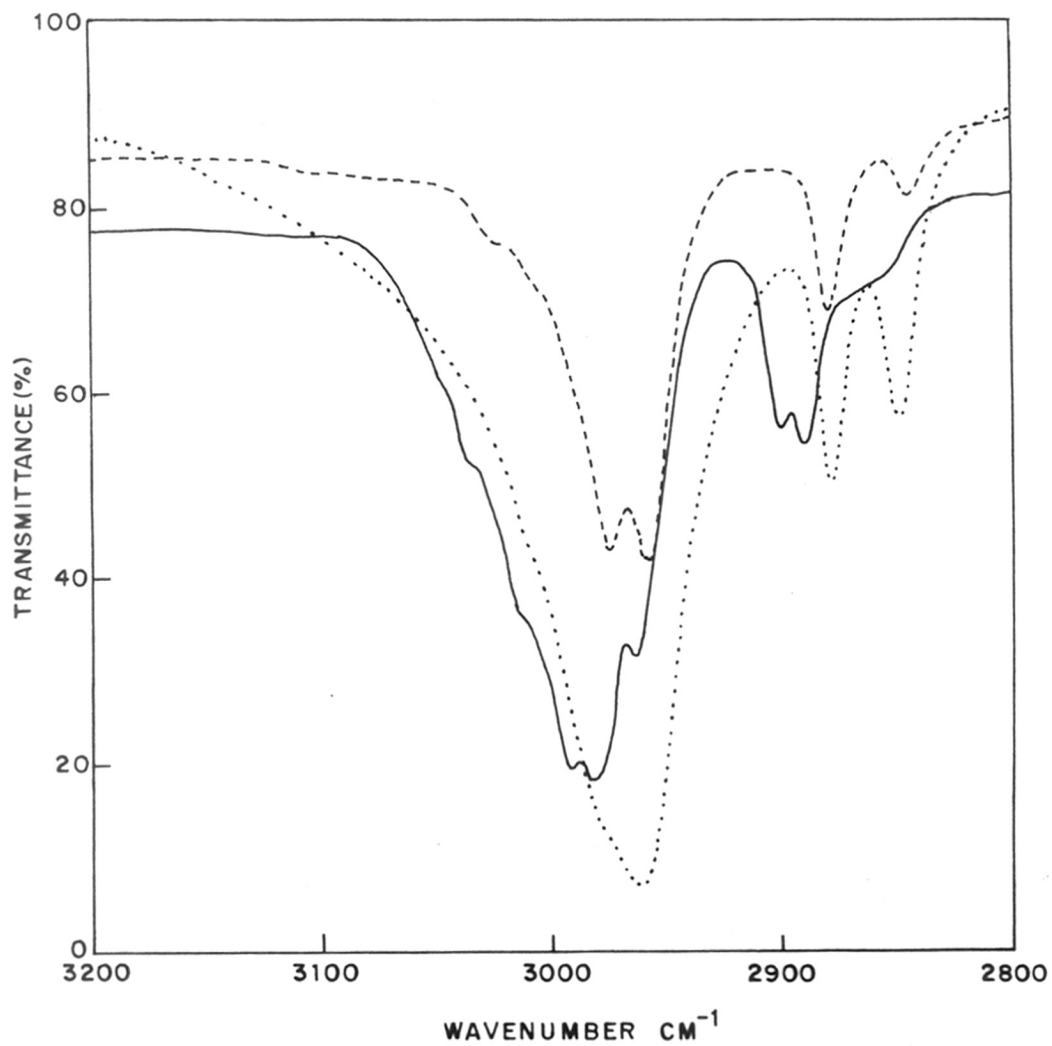


FIG. 1 IR SPECTRA OF 1,2,DICHLOROETHANE  
Vapour (—) , CCl<sub>4</sub> Solution (----)  
Liquid (.....)

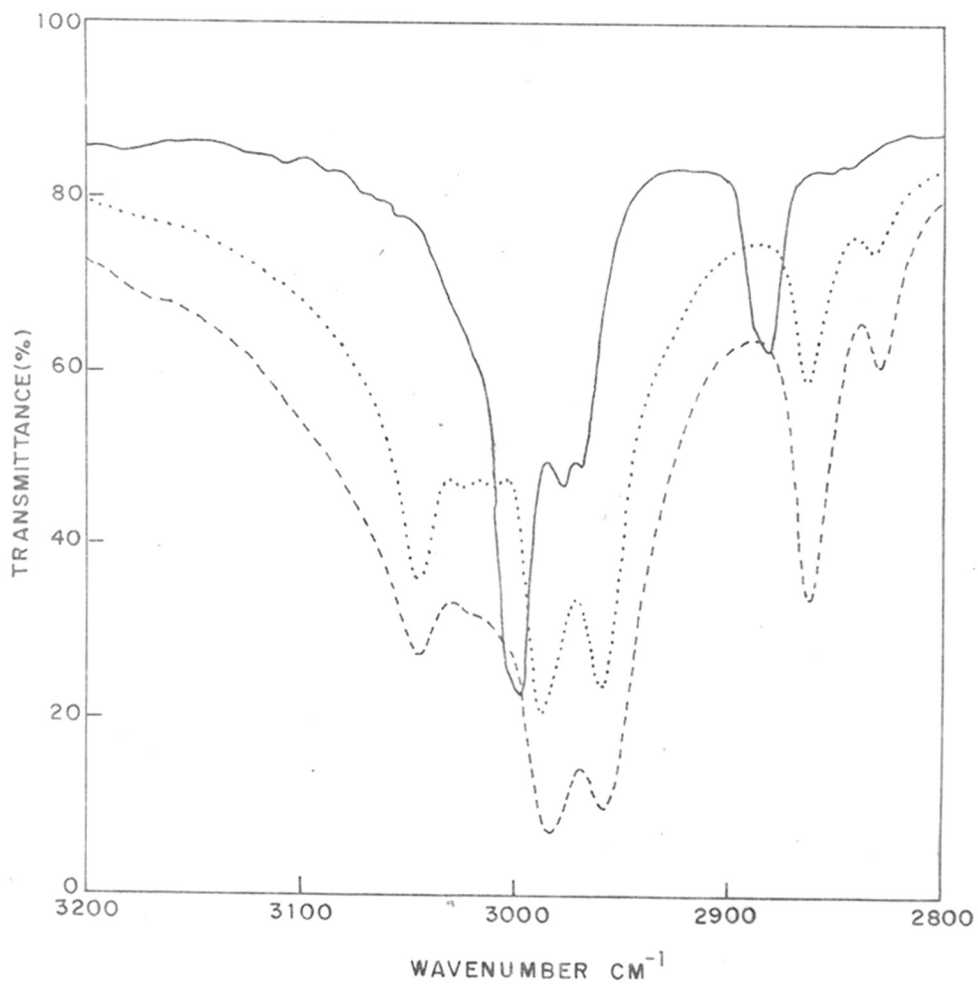


FIG. 2 IR SPECTRA OF 1,2,DIBROMOETHANE  
Vapour (—), CCl<sub>4</sub> Solution (----)  
Liquid (.....)

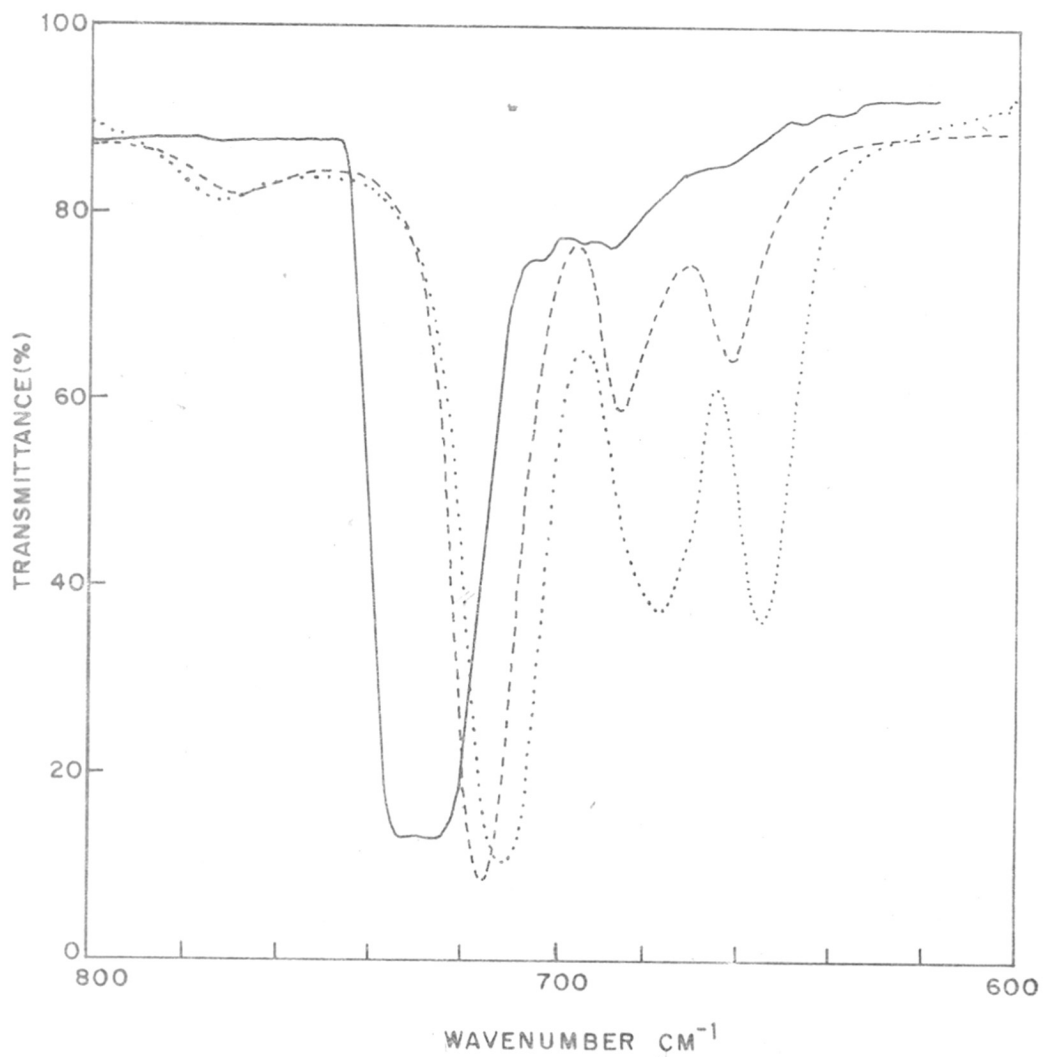


FIG.3 IR SPECTRA OF DICHLOROETHANE  
Vapour (—) , CS<sub>2</sub> Solution (----)  
Liquid (.....)

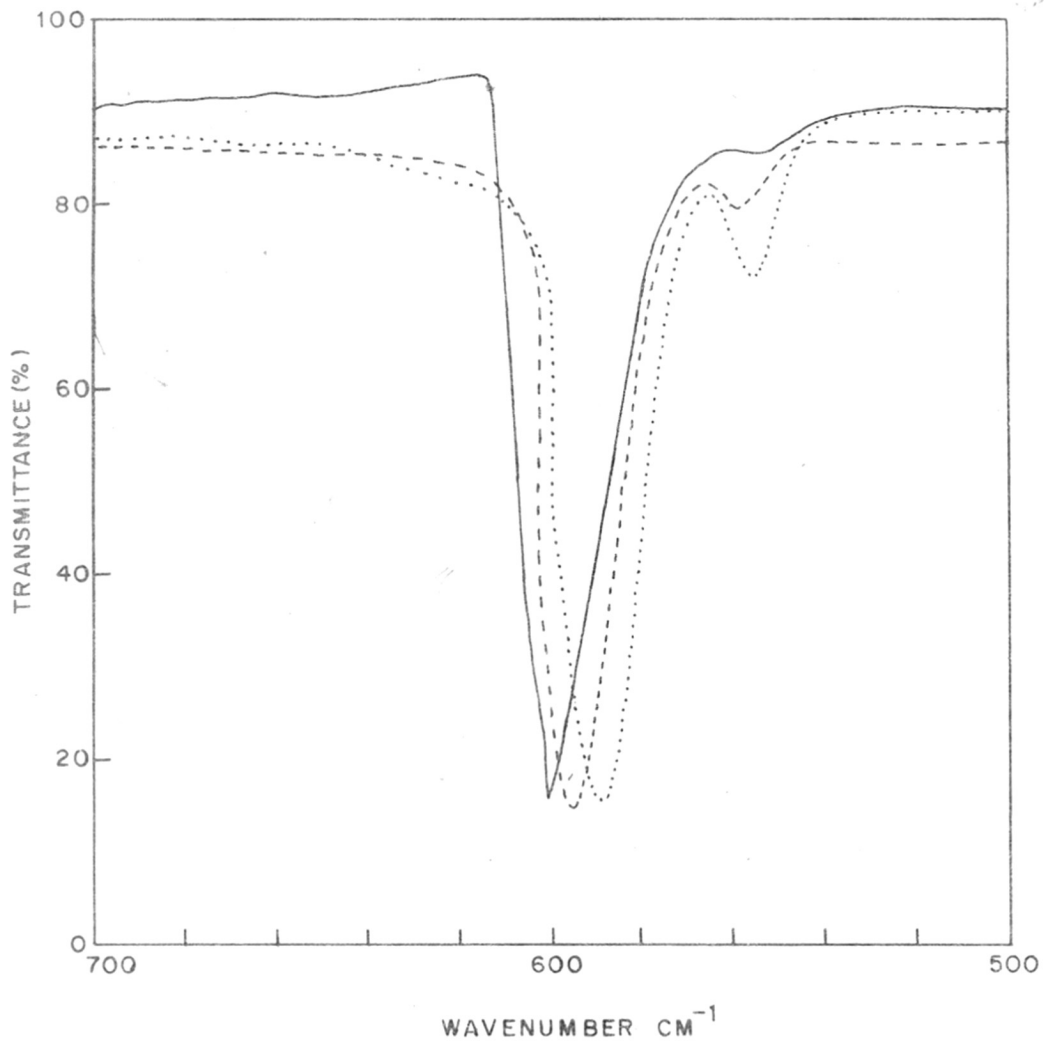


FIG. 4 IR SPECTRA OF DIBROMOETHANE

Vapour (—), CS<sub>2</sub> Solution (----)

Liquid (.....)



TABLE I : INFRARED SPECTRAL BANDS OF 1,2-DICHLORO ETHANE

Liquid		Vapour		Solution CCl <sub>4</sub> /CS <sub>2</sub>		Assignment
Fre- quency	Trans/ gauche	Fre- quency	Absor- bance	Fre- quency	Absor- bance	Trans/ gauche
3636	sh					
3008	sh					
2992	s					
2972	sh 0.47	1.8	0.65	2974	m 0.29	2.7
2962	s 0.77/3		0.30/3	2958	m 0.32/3	
2900	w					
2878	m			2880	m	
2848	m			2844	m	
710	vs 0.95	2.5	0.60	710	vs 0.97	6.1
676	m 0.38		0.03	676	w 0.16	
656	m 0.40	2.37		656	w 0.19	5.1

} CH<sub>2</sub> asym. trans.

} CH<sub>2</sub> asym. gauche

} CH<sub>2</sub> sym.

} C-Cl trans.

} C-Cl gauche.

} C-Cl gauche

TABLE - II - INFRARED SPECTRAL BANDS OF 1,2-DIBROMO ETHANE

Liquid			Vapour			Solution			Assign. men.
Frequency	Trans/ Gauche	Absorbance	Frequency	Trans/ Gauche	Absorbance	Frequency	Trans/ Gauche	Absorbance	
3048 m			3044 s						
3029 w						2984 vs		1.08	3.5
3015 w									
2993 s		0.60	2990 s		0.57				
				3.3		2975 m			
2960 s		0.54/3				2962 m		0.24/3	
2864 m						2878 m			
2832 w									
590 s		0.74/2	4.2		0.79/2	597 s	11.6	0.78/2	12.2
556 w		0.087			0.034	550 w		0.032	

} CH<sub>2</sub> asym. trans.  
 } CH<sub>2</sub> asym. gauche  
 } CH<sub>2</sub> sy  
 } C-Cl trans.  
 } C-Cl gauche

CHAPTER - V

1,2-DIAMINO AND DIHYDROXY ETHANES

V :            A : 1,2-DIAMINO ETHANE

The infrared spectra of ethylene diamine in the liquid, solution and gaseous states in the region 2700-3500  $\text{cm}^{-1}$  were taken (Fig. 5) and the absorption frequencies and their possible assignments are given in Table. The NH stretching bands were essentially similar in all the three states having single asymmetric and symmetric ~~sb~~ modes differing slightly in their frequencies due to intra/intermolecular hydrogen bonding. An overtone absorption of the  $\text{NH}_2$  deformation mode was also found in the region 3215-3170  $\text{cm}^{-1}$ . Single nearly symmetric bands were <sup>also</sup> found for the  $\text{CH}_2$  symmetric and asymmetric stretching modes in the region 2925-45 and 2850-2875  $\text{cm}^{-1}$ .

Essentially a single set of  $\text{NH}_2$  and  $\text{CH}_2$  stretching bands in the three states suggest that *only one* type of rotational isomer is present. Electron diffraction studies<sup>12</sup> of ethylene diamine in the vapour state had shown that nearly all the molecules are in the gauche form in the vapour at 50-120°C. On the other hand, a trans conformation was found to be present in the solid state by x-ray diffraction studies<sup>13</sup> of single crystals. An infrared analysis of the solid<sup>16</sup> had shown four bands for the  $\text{CH}_2$  stretching modes at 2930, 2917, 2914 and 2860  $\text{cm}^{-1}$  and a series of 5 bands in the NH stretching region at 3160-3340  $\text{cm}^{-1}$ . While multiplicity of NH stretching modes could result from intermolecular hydrogen bonding, the number of  $\text{CH}_2$  stretching modes would reflect the symmetry of the species in the solid. Two out of the four  $\text{CH}_2$  stretching

frequencies in the solid are similar to those found in the liquid/solution states. The bands at 2917 and 2914  $\text{cm}^{-1}$  which had no equivalent in the liquid/solution can be considered characteristic of the trans species. Thus trans species are completely absent in solution and gaseous states.

In order to find out whether ethylene diamine molecules in the gauche form are intramolecularly hydrogen bonded in dilute solution, we compared its spectrum with that of n-propylamine and found that the NH frequencies and the nature of the bands are nearly the same ruling out any intramolecular hydrogen bonding in the former. Bellamy and Williams<sup>35</sup> had found from a detailed analysis of the NH stretching frequencies of primary amines in solution the following relationship

$$345.53 + 0.876 \nu_s = \nu_{as}$$

holds for the free asymmetric and symmetric stretching frequencies. For ethylene diamine, the agreement with  $\nu_{as}$  calculated was within 8  $\text{cm}^{-1}$ . This again suggests that intramolecular hydrogen bonding is absent in this molecule.

A band near 2800  $\text{cm}^{-1}$  is found in many compounds containing nitrogen adjacent to a  $\text{CH}_2$  or  $\text{CH}_3$  group and it has been shown<sup>36</sup> to arise from an interaction between the localised lone pair electron of nitrogen and CH bonds lying trans to it. Assuming a staggered configuration for adjacent  $\text{CH}_2$  and  $\text{NH}_2$  groups in ethylene diamine, it can be seen that if intramolecular hydrogen bonding takes place, one of the CH bonds of the  $\text{CH}_2$

group has to be trans to a lone pair of electrons on the nitrogen. The absence of such a band near  $2860\text{ cm}^{-1}$  in dilute solution of ethylene diamine is thus clear indication of the absence of intramolecular hydrogen bonding in ethylene diamine in spite of the gauche conformation of the two C-N bonds with respect to the central C-C bond. The conformations of the  $\text{NH}_2$  groups under such conditions where none of the CH bonds of the two  $\text{CH}_2$  groups is trans to lone pairs on nitrogens would be when  $\text{CH}_2$  and  $\text{NH}_2$  groups are trans to one another. Such a conformation has been found in one of the two conformations in the solid, though here the two  $\text{CH}_2$  groups themselves are trans to one another.

//  
Krueger however concluded from absorbance ratios of a series of alkyl diamines [ $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ ,  $n = 2-6,10$ ] that some intramolecularly hydrogen bonded species might exist in dilute  $\text{C}_2\text{Cl}_4$  solution. Since the dipole moment of ethylene diamine in benzene did not show any temperature dependence, Kimura et al concluded that ethylene diamine does not form intramolecular hydrogen bond in solution.

The present studies thus show that ethylene diamine exists nearly entirely in the gauche form with no intramolecular hydrogens bonding in dilute carbon tetrachloride solution. In the vapour also, the gauche species are exclusively found. In the liquid however some small amount of trans species may be found as the bands in the  $\text{CH}_2$  stretching region were slightly broader.

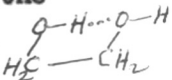
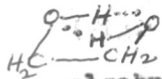
V :            B : 1,2-DIHYDROXY ETHANE

The hydroxyl bands of ethylene glycol in dilute carbon tetrachloride solution is shown in Fig. 6. The various band characteristics like frequency half band width, band area and the concentrations of the two types of hydroxyl groups calculated using the integrated absorption intensities of the free and intramolecularly hydrogen/<sup>bonded</sup> species in methanol and methoxy ethanol<sup>11</sup> respectively ( $4.7$  and  $6.4 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-2}$ ) are given in Table. The two bands were separated using graphical resolution taking into account the expected differences in the half band widths of the free and intramolecularly hydrogen bonded hydroxyl groups.

The two hydroxyl band frequencies observed in the present case are in agreement with those reported (3466, 3604). Krueger and Mettee<sup>26</sup> observed an additional band ( $3614 \text{ cm}^{-1}$ ) at lower temperature very close to the intramolecularly hydrogen bonded hydroxyl band which was ascribed specifically to the bicyclic intramolecularly hydrogen bonded species. It was not possible to locate this band at  $30^\circ\text{C}$ , due to possible merging with intramolecularly hydrogen bonded hydroxyl band at  $3606 \text{ cm}^{-1}$ . The half band widths of the free and intramolecularly hydrogen bonded hydroxyl bands were in agreement with reported values<sup>11</sup>.

The calculated concentrations of the free ( $1.5 \times 10^{-3} \text{ M}$ ) and intramolecularly hydrogen bonded hydroxyl species ( $2.1 \times 10^{-3} \text{ M}$ ) for a solution concentration of  $1.9 \times 10^{-3} \text{ M}$  shows that nearly all the molecules are intramolecularly hydrogen bonded in solution and some of them may be doubly hydrogen bonded species. It is found that in methoxyl ethanol, the relative proportions of

intramolecularly hydrogen bonded and free species were 87% and 13% respectively. On this basis, for a dihydroxyl compound like ethylene glycol, the presence of all the species in intramolecularly hydrogen bonded form would not be unexpected. Thus the presence of a possible species with both the hydroxyl groups free can be ruled out. Regarding the doubly hydrogen bonded hydroxyl species, there is obviously no other alternative explanation for the lower free hydroxyl concentration in solution.

Assuming that ethylene glycol consists of only the singly (A) and doubly (B) hydrogen bonded hydroxyl species  ) their concentrations were calculated as follows using algebraic equations 

$$A + B = 1.9$$

$$A = 1.4$$

$$A + 2B = 2.1$$

The best values calculated from these equations gave 1.3 and  $0.4 \times 10^{-3}$  M as the concentrations of the singly and doubly intramolecularly hydrogen bonded species, so that one can conclude that in dilute solution nearly 25% of the species of ethylene glycol <sup>exists</sup> as the hydrogen bonded box type monomer and 75% singly hydrogen bonded species.

Our results are in general agreement with those of Krueger and Mettee<sup>26</sup> who had earlier concluded that only intramolecularly hydrogen bonded species existed in dilute solution of ethylene glycol and doubly hydrogen bonded species may also be present. However, they had not determined the



relative proportions of the two species. Busfield et al<sup>9</sup> however concluded from studies of a series of glycols ( $\text{HO}(\text{CH}_2)_n\text{OH}$ ,  $n = 2-6$ ) that in dilute solution of ethylene glycol there are only singly intramolecularly hydrogen bonded species and free species where both the hydroxyl groups are free. This conclusion was arrived at by assuming that the molar extinction coefficients of free and intramolecularly hydrogen bonded hydroxyl groups were the same. The reported values<sup>11</sup> of the integrated absorption intensities of the free (4.7) and intramolecularly hydrogen bonded five membered ring (6.4) hydroxyl groups show that such an assumption is unwarranted.

The structure of the bicyclic doubly intramolecularly hydrogen bonded species is unusual from the point of view of the relative orientation of the hydroxyl bond with respect to the lone pair direction. In the gauche conformation of the C-O bonds, the bond distance between the oxygen atoms is well within the limits for hydrogen bonding (3.4Å). If the two hydrogen bonds formed in the molecule are similar, then the angle between the O-H bond and the oxygen lone pair orbital would be much smaller (less than  $90^\circ$ ) than normally observed. It can be concluded that weak hydrogen bonding interaction can take place in spite of adverse hydroxyl bond orientation with respect to the lone pair orbital direction. This can be understood to some extent from the electrostatic nature of hydrogen bond where the positive and negative charges on the proton and lone pair electrons play the predominant role along with the distance between them.

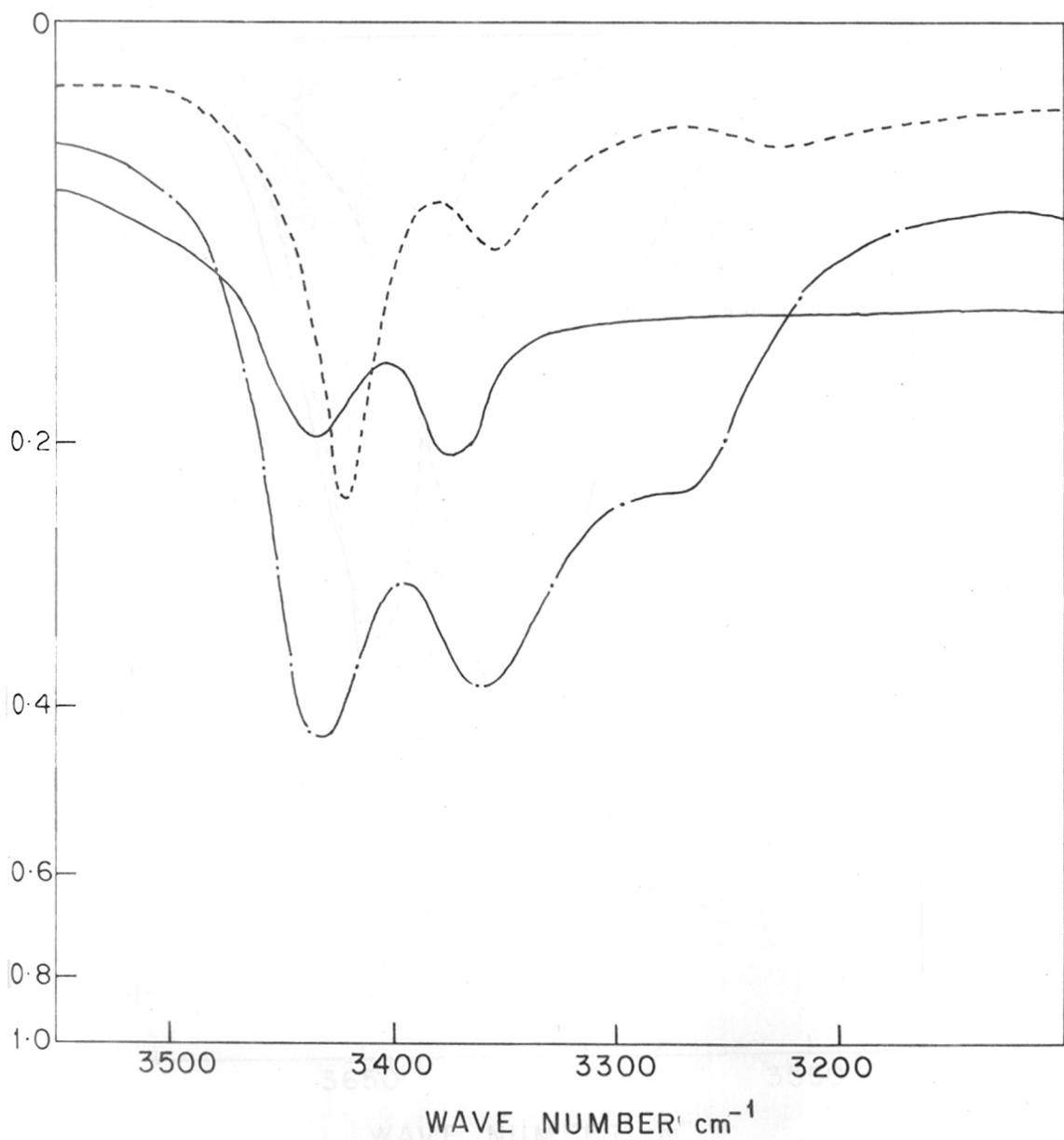


FIG.5 IR SPECTRA OF ETHYLENE DIAMINE  
GAS (—), LIQUID (— · —), SOLUTION (-----)

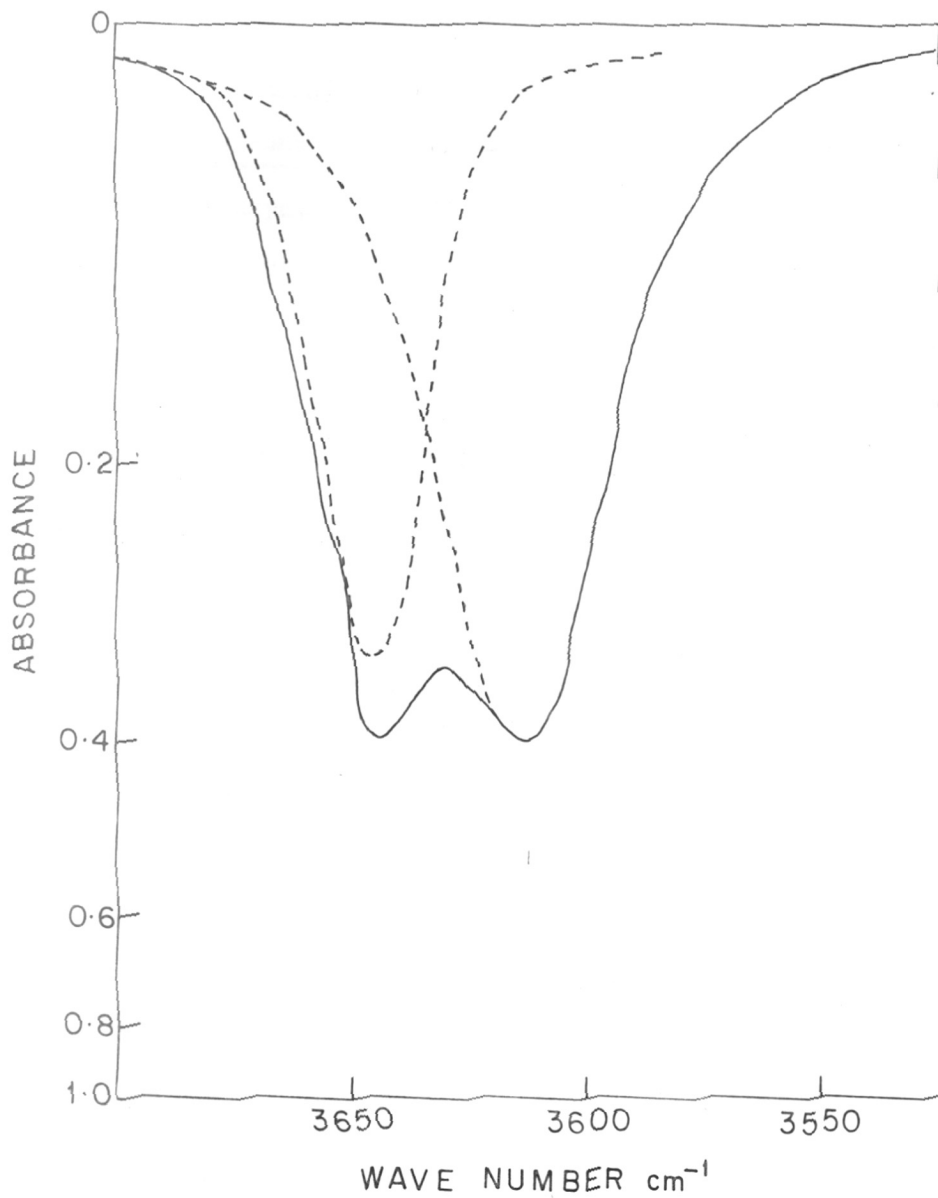


FIG. 6 IR SPECTRUM OF ETHYLENE GLYCOL IN SOLUTION

TABLE - III

IR SPECTRAL BANDS (CM<sup>-1</sup>) OF ETHYLENE DIAMINE

<u>Assignment</u>	<u>Liquid</u>	<u>Vapour</u>	<u>Solution in CCl<sub>4</sub></u>
$\nu$ NH asym.	3365 s	3440 w	3398 m
$\nu$ NH sym.	3285 s	3385 w 3300 w	3330 w,b
2 x $\nu$ NH	3190 m	3215 w	3170 w
$\nu$ CH <sub>2</sub> asym.	2945 s	2950 s	2925 vs
$\nu$ CH <sub>2</sub> sym.	2875 s	2870 s	2850 vs
	2765 w	2770 w	2730 w

TABLE - IV

HYDROXYL BAND INTENSITIES OF ETHYLENE  
GLYCOL IN CARBON TETRACHLORIDE

Solution concentration  $1.9 \times 10^{-3}$  M  $l = 3.55$  cm.

<u>Frequency</u> cm <sup>-1</sup>	<u><math>\Delta\nu</math></u> cm <sup>-1</sup> 1/2	<u>Area</u> cm <sup>-1</sup>	<u>Hydroxyl group con- centration</u>
3637	25	24.4	$1.5 \times 10^{-3}$
3606	35	47.2	$2.1 \times 10^{-3}$

CHAPTER - VI

CH<sub>2</sub> INTENSITY MEASUREMENTS AND GENERAL DISCUSSION

VI :            A : INTEGRATED ABSORPTION  
                  INTENSITY OF CH<sub>2</sub> GROUP

The integrated absorption intensities of the CH<sub>2</sub> stretching modes (Fig. 7) calculated from the total band area for the 1,2-dihalo(Cl,Br), diamino and dihydroxy ethanes are given in Table V. It is clear the CH<sub>2</sub> intensity (unit) values for the amino and hydroxy derivatives are close to that in alkanes while in the halo derivatives it is an order of magnitude smaller. We had seen from the conformational studies of the dihalo, diamino and dihydroxy ethanes reported in chapters IV and V that the trans species were predominant in the two halo derivatives in dilute solution while the gauche species were predominant in the hydroxy and amino derivatives. The trans species of the symmetrically disubstituted ethanes have a centre of symmetry and therefore of the four CH<sub>2</sub> stretching modes, two are inactive in infrared, but active in Raman spectra and vice versa. In the gauche species on the other hand all the four CH<sub>2</sub> stretching modes are active in infrared and Raman simultaneously. Thus if the intensity parameters of the trans and gauche species are assumed to be the same, then a reduction by half in the CH<sub>2</sub> intensity of the trans dominant halo ethanes can be expected.

Early observations on alkanes containing hydroxy, methoxy and oxymethylene groups had shown<sup>29</sup> considerable reduction in the methyl and methylene group intensities compared to those in pure alkanes. A comparison of the absolute

intensities of the  $\text{CH}_3$  stretching modes of acetone vapour<sup>31</sup> and hydrocarbons showed that the unit intensity of the  $\text{CH}_3$  group in the former was smaller than in the latter by a factor of four. The methyl intensity in halomethanes also showed<sup>37</sup> marked reduction compared to the intensity in methane. Integrated absorption intensities of the methyl groups in various chloro methyl silanes were found<sup>32</sup> to decrease with increasing chlorine substitution from 570 in tetramethyl silane to 25 in trichloromethyl silane. Attempts have been made to interpret intensity data in terms of inductive, mesomeric or resonance and steric influences of the substituent group; so also to correlate the band intensity variation with the electronegativity of the substituent group. Higuchi et al<sup>33</sup> have measured the intensities of the asymmetric stretching and symmetric deformation modes of  $\text{CH}_3$  group when it is directly bonded to a variety of groups like  $\text{CN}$ ,  $\text{SO}$ ,  $\text{NO}_2$ ,  $\text{CCl}_3$  halogens,  $\text{NCS}$ ,  $\text{NCO}$ , etc. They found a steady decrease in  $\text{CH}_3$  stretching intensity with increase in Taft parameters in the case of the halo derivatives. In the other substituents, the order<sup>was</sup> reverse. Their results also showed that the  $\text{CH}_3$  stretching frequencies decreased monotonously in an approximately exponential fashion with increase in inductive effect except in the case of the halo derivatives where the order was reversed which was interpreted as resulting from the delocalisation of n-electrons on halogen atoms.

It is clear from the present studies that the integrated absorption intensity of the  $\text{CH}_2$  group is not directly related to the electronegativity of the substituent group/atoms

which in the present case, are only marginally different and does not follow any order (O, 3.5; Cl, N 3.0; Br, 2.8) while the intensity variation was at least 5 times between the halo and the amino/hydroxy derivatives. If steric factor in terms of the Vanderwaals radius was an important parameter in the intensity function, then the appreciable differences in them (Br, 1.95A; Cl, 1.8; N, 1.50; O, 1.4) could be responsible for the large difference. This factor is indeed responsible for the predominant trans configuration of the halo derivatives of ethane.

VI :        B : CONFORMATIONAL BEHAVIOUR OF 1,2-DIBROMO,  
             DICHLORO, DIAMINO AND DIHYDROXY ETHANES -  
             A DISCUSSION

The conformational behaviour of single bonded compounds  $XCH_2CH_2X$  is largely determined by (a) electrostatic interactions arising from mutual repulsion of C-X dipoles where X = Br, Cl,  $NH_2$ , OH, in the present series, (b) steric repulsion hindering rotation around C-C which depends on the sizes of X and (c) stabilization resulting from intramolecular hydrogen bonding if present.

Our studies had clearly established that the two haloethanes, dibromo and dichloro ethanes existed predominantly as trans species in dilute solutions while the diamino and dihydroxy ethanes were present mostly as the gauche species. In order to understand this behaviour the electrostatic



interactions resulting from mutual repulsions of C-X dipoles was considered. The C-X dipoles depend largely on the electronegativity of the X atom which in the present series varied in such a way (Br, 2.8; Cl, N, 3.0; O, 3.5) that it did not support the observed results. Thus the role of repulsive interactions arising from C-X dipoles is not a major factor in deciding the conformational preference in the present compounds.

With regard to the steric repulsions hindering rotations which depends on the sizes of X, the Vanderwaals radii of the substituent atoms were considered (Br, 1.95A; Cl, 1.8; N, 1.6 and O, 1.42). It is clear that the radii are markedly large for the two halo derivatives which were found to exist predominantly in the trans conformation where steric repulsions are least. The importance of the steric factor is further confirmed from the reported studies on 1,2-difluoroethane<sup>38</sup> which was found to exist predominantly in the gauche conformation. The Vanderwaals radius of fluorine (1.35A) is comparable to that of oxygens. Thus the importance of the steric factor in determining conformational preference is established. The trans conformer obviously has less steric restrictions than the gauche conformer.

Regarding the stabilisation of the gauche form due to hydrogen bonding, we found no evidence for intramolecular hydrogen bonding in ethylene diamine, though in ethylene glycol there was a weak intramolecular hydrogen bond in the predominant gauche

species. But the preference for gauche species is obviously present in most of the oxygen and nitrogen substituted derivatives of ethane even without intramolecular hydrogen bonding. Thus dimethoxy ethane<sup>39</sup>, was found to exist predominantly in the gauche conformation in solution; the  $\text{OCH}_2\text{CH}_2\text{O}$  group in polyoxyethylenes<sup>40</sup> was found to prefer a gauche conformation in solution. Though the reasons for this preference has not been fully understood, the smaller Vanderwaals radii are responsible for reducing the steric repulsion in the gauche conformation.

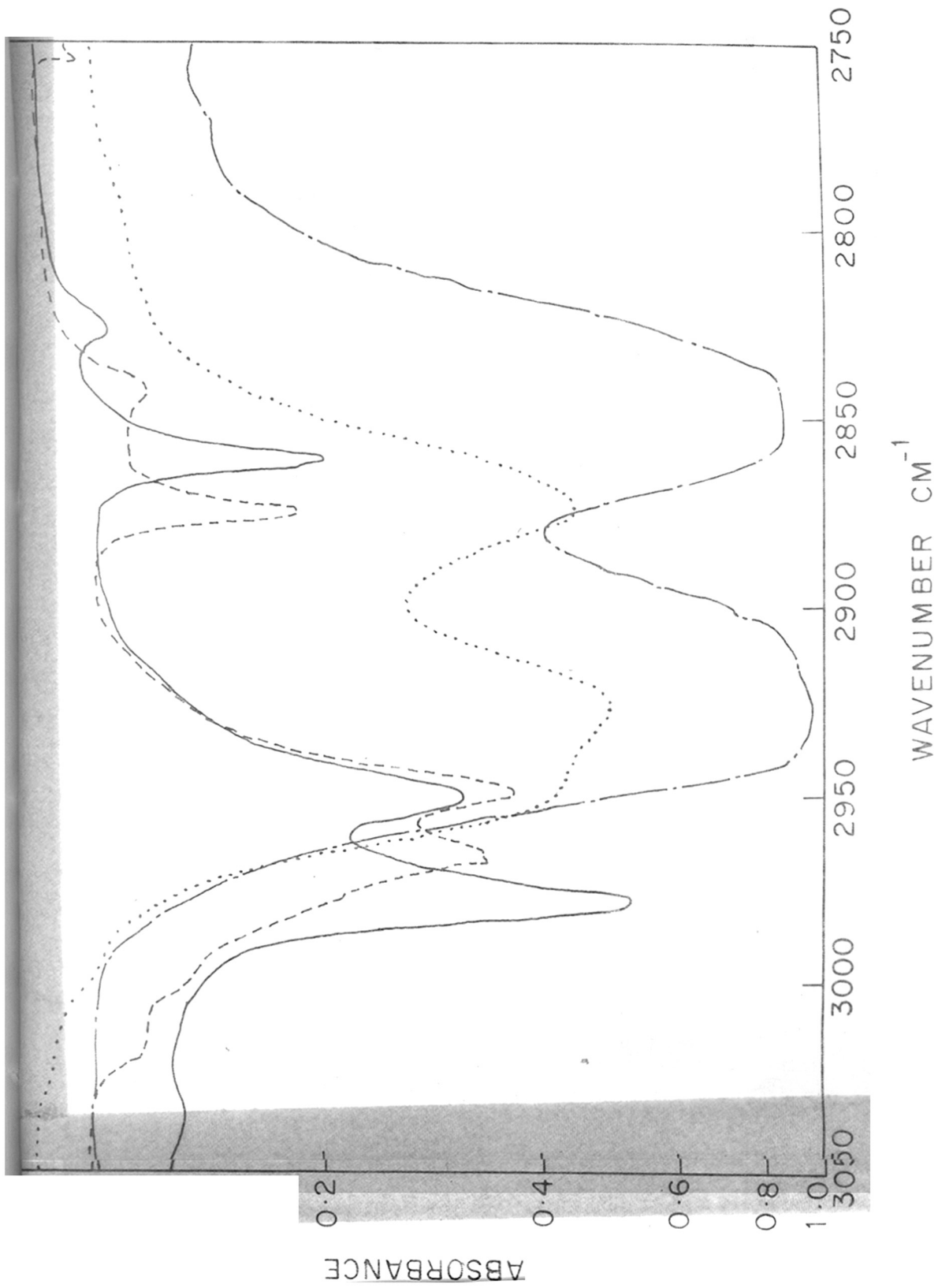


FIG. 7

TABLE - V

INTEGRATED ABSORPTION INTENSITIES OF CH<sub>2</sub>  
STRETCHING MODES IN XCH<sub>2</sub>X COMPOUNDS

X	Concentration mole	Path length cm	Band area cm <sup>-1</sup>	Integrated absorption intensity x 10 <sup>-3</sup>	
				Observed	Reported <sup>29</sup>
Cl	0.47	0.05	45.0	1.92	
Br	1.24	0.05	50.8	0.82	
OH	0.002	3.55	104.6	14.7	
NH <sub>2</sub>	0.0178	0.80	251.8	17.7	
CH <sub>3</sub>	-	-	-	-	15.3

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