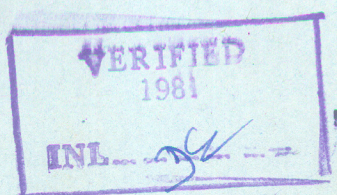
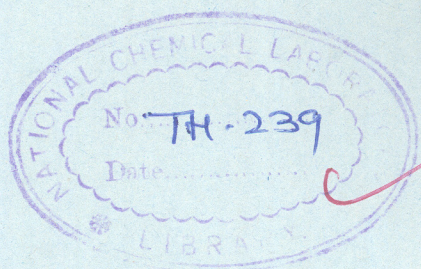


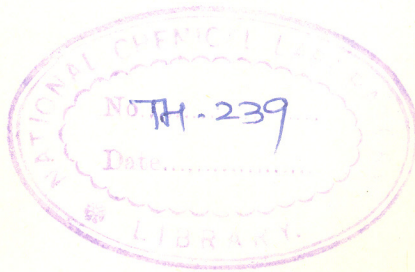
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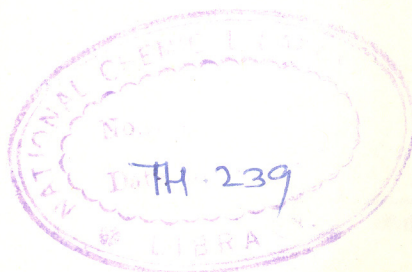
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INFRARED SPECTRA AND HYDROGEN BONDING  
OF MONOALKALI SALTS OF ALKYL MALONIC  
AND SUCCINIC ACIDS

A THESIS SUBMITTED TO THE UNIVERSITY OF  
POONA FOR THE DEGREE OF MASTER OF SCIENCE  
[CHEMISTRY], PARTLY BY PAPERS, PARTLY BY  
RESEARCH



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BY

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CHAPTER - I

I N T R O D U C T I O N



Studies of the ionisation constants of acids and bases provided one of the early evidences for polar, steric and resonance effects in molecules. If the electron density in the vicinity of an ionisable proton is decreased, on simple electrostatic theory, it should be easy to remove the proton. Thus the introduction of a substituent carrying an electrical charge markedly affects the acid and base strength. The effect of the charge on the ionization constant decreases rapidly with increasing distance from the ionisable proton. An electropositive or electronegative group in the  $\alpha$  position can also result in considerable change in the strength of the acid and base. The shift of the electrons of the intervening bonds under the influence of a substituent is termed the inductive effect of the substituent.

In dibasic acids, in the absence of electrostatic interaction the ratio of dissociation constants  $k_1/k_2$  should be 4. However, this ratio was found to be much greater even in simple acids. Thus in malonic, succinic and fumaric acids, they are approximately 700, 192 and 23.2 respectively. In order to explain the effect of a group at considerable distance from the ionization centre where the inductive effect will be small, a direct electrostatic interaction through the solvent has also been suggested.

In substituted dibasic acids like malonic, succinic etc.  $k_1/k_2$  showed the expected moderate changes on methyl substitution (dimethyl malonic acid 783, tetramethyl succinic acid 6130) but unusually high values were found in higher alkyl substituted derivatives (diethyl, di-*n*-propyl malonic acids 121000, 277000, tetraethyl succinic acid 45710 respectively). It was evident that these large values were not due to electrostatic influence of the charge of the carboxylate ion brought about by alkyl substituents.

McDaniel and Brown<sup>1</sup> first suggested that intramolecular hydrogen bonding of the carboxylic hydrogen to the carboxylate ion might be responsible for the resistance to dissociation of the second carboxylic hydrogen and therefore to high dissociation constant ratio  $k_1/k_2$  found in these substituted malonic and succinic acids. Here the steric requirements of two ethyl groups<sup>2</sup> on a single carbon atom (as in diethyl malonic acid) are quite large so that they cannot lie in a single plane. The formation of intramolecular hydrogen bond between the COOH and COO<sup>-</sup> groups might relieve a good portion of this strain.

Eberson has studied the hydrogen bonding in certain highly alkylated succinic acids and their monoanions using infrared<sup>3</sup> and proton magnetic resonance<sup>4</sup> spectroscopic techniques. Lower carbonyl stretching frequency of the acid salts in methanol



solution as compared to in KBr matrix was ascribed to an intramolecular hydrogen bonding. The carbonyl band intensity in the monoanion was smaller than in the parent acid. The large value of PMR chemical shift of OH group in tetraalkylated succinic acid monoanion in dimethyl sulphoxide (DMSO) also suggested strong intramolecular hydrogen bonding.

From thermodynamic data Das and Ives<sup>5</sup> concluded that hydrogen malonate ion exists as a strongly intramolecularly hydrogen bonded species in water. However, Lloyd and Prince<sup>6</sup> observed that there is only a weak asymmetrical hydrogen bonding in sodium salt of malonic acid in water.

Akermark<sup>7</sup> from a study of pinnaric acid derivatives suggested that the strength of hydrogen bonds can be determined from the shift in the carbonyl stretching frequency in KBr or Nujol from that in tetrahydrofuran solution. A small shift is indicative of a strong intramolecular hydrogen bond.

Chapman et al.<sup>8</sup> studied the infrared spectra of malonic, di-n-propyl malonic acid and their mono and dialkali metal salts in aqueous solution. Assuming that the strength of hydrogen bonding is reflected in the relative lowering of the bonded carbonyl stretching frequency and increase in the asymmetric stretching frequencies of the free and bonded carboxylate groups, they concluded that the monoanion of di-n-propyl malonic acid exists as a strong intramolecular hydrogen

4

bonded species. They found no evidence for strong symmetrical hydrogen bonding in aqueous solution of potassium hydrogen malonate in contradiction to the conclusion drawn from thermodynamic data<sup>5</sup>.

Glasoe<sup>9</sup> found considerable difference in hydrogen bonding in the diethyl malonate acid anion compared to the ethyl malonate monoanion from infrared spectral measurements in water.

Hanrahan<sup>10</sup> has studied malonic, ethyl malonic and diethyl malonic acid in KBr matrix, D<sub>2</sub>O and dioxane. His data showed a trend in the opposite direction to that found by Akermark<sup>7</sup> and concluded that this test is probably not applicable to malonic acid derivatives. The larger frequency shift in diethyl malonate monoanion in D<sub>2</sub>O was regarded as evidence for a strong hydrogen bond. The frequency shifts in the monoanions of other acids were smaller ruling out strong hydrogen bonding in them.

Miles et al.<sup>11</sup> studied the reaction rates of the ionisable protons in aqueous solution of dialkyl substituted malonic acids and found that relatively slow reaction rates of the proton from the second COOH group could be ascribed to its involvement in a strong hydrogen bonding with the carboxylate ion.



Evans and Goldstein<sup>12</sup> had investigated the hydrogen bonding in malonic, methyl malonic and isopropyl malonic acid from proton magnetic resonance spectra in water at different pH. The vicinal coupling constant in isopropyl malonic acid showed variation with pH and it was minimum at pH 4 which is approximately the point of half neutralization. Since the vicinal coupling is dependent on dihedral angle it was interpreted as indicative of the presence of a strong intramolecular hydrogen bonding between the COOH and COO<sup>-</sup> groups. Under the same conditions in the methyl derivative, the vicinal coupling constant remained independent of pH.

The above review shows that the second dissociation constant values of alkyl substituted malonic and succinic acids is connected to the nature of hydrogen bonding in their monoalkali salts though a clear picture has not emerged. Since aqueous system is not favourable for study of hydrogen bonding particularly to determine its inter or intramolecular nature, we have in the present work investigated the infrared spectra of monoalkali salts of a few monoalkyl, dimethyl, diethyl and di-n-propyl malonic acids and tetramethyl and tetra-n-propyl succinic acids in the solid state and in DMSO solution to establish the nature of hydrogen bonding in them. We have also taken proton magnetic resonance spectra in DMSO to obtain additional evidence to support the infrared results.

Previous infrared studies<sup>13</sup> and recent X-ray<sup>14</sup> and neutron diffraction<sup>15</sup> investigations showed that in solid potassium hydrogen malonate there is a strong intermolecular symmetrical hydrogen bonding with an O-H...O distance of 2.46Å. Very recently, we had found that the infrared spectrum<sup>16</sup> of solid sodium hydrogen malonate was vastly different from that of potassium hydrogen malonate and the hydrogen bonding in the former is weaker and asymmetric in nature. In DMSO the hydrogen bonding in both the sodium and potassium hydrogen malonate was however found to be similar and asymmetric as in the solid sodium hydrogen malonate.

Albertson et al. have recently found from detailed X-ray<sup>17</sup> and neutron diffraction<sup>18</sup> investigations an intermolecular asymmetric hydrogen bond in the monosodium and monopotassium salts of oxydiacetic acid and symmetric hydrogen bond in the rubidium, caesium and thallium salts. An increase in the symmetry of the structure resulted in going from potassium to rubidium salt, brought about a change from an asymmetric to a symmetric hydrogen bonding. We have therefore extended our infrared studies in the present work to other alkali ions, lithium, rubidium, caesium with a view to investigate the role of ionic radius on the nature of hydrogen bonding in monoalkali salts of malonic acid.



CHAPTER - II

INFRARED SPECTROSCOPY

## 1. Molecular spectra

The total energy of a molecule can be expressed as the sum of its electronic, vibrational and rotational energies (excluding translational energy)

$$E = \epsilon_e + \epsilon_v + \epsilon_R$$

Since the magnitudes of these energy terms are very different from one another (electronic 4, vibrational 0.2 and rotational 0.01 eV respectively) changes can be assumed to occur independently in them (Born-Oppenheimer approximation). While ultraviolet and visible radiation can bring about changes in the electronic energy states, infrared and microwave radiations induce changes in the vibrational and rotational energy states respectively.

## 2. Vibrational spectra

According to quantum theory, a molecule can possess only certain energy states (allowed) and transitions take place between these states. The vibrational energy of a molecule is given by:

$$\epsilon_v = (v + \frac{1}{2}) h \nu_e - (v + \frac{1}{2})^2 h \nu_e x_e$$



where  $V$  = vibrational quantum number, 0, 1, 2 .... etc.

$\nu_e$  = vibrational frequency.

$\chi_e$  = anharmonicity constant.

Since the difference in energies between the vibrational ground state and first excited state is high compared to  $kT$  at room temperature, according to Boltzman's distribution law

$$N = N_0 e^{-\Delta E/kT}$$

the excited state is very sparingly populated ( $\sim 1$  in 10,000). Under such conditions, transitions to excited vibrational state by absorption of radiation takes place readily. Infrared spectrum is therefore conveniently obtained as an absorption spectrum.

For vibrational transition to take place, there should be a change in the dipole moment of a bond during the vibration. Homopolar diatomic molecules like  $H_2$ ,  $N_2$ ,  $O_2$ , etc. and certain vibrations in symmetrical molecules where no change in dipole moment takes place during the vibration do not therefore give rise to infrared absorptions. Though the transitions from the ground state to the first excited state is the most probable, overtones and combination modes are also observed.

### 3. Vibrational frequencies

#### (A) Diatomic molecules

Before analysing the vibrations of a complex molecule, let us consider the interactions of a heteropolar diatomic molecule X-Y. The atoms in it are never stationary and the distance between them is a periodic function of time. This molecule is capable of absorbing infrared frequencies which correspond to the frequencies of its different molecular vibrations. For a diatomic molecule the vibration is due to a stretching of bond X-Y only and is given by:

$$\nu = \frac{1}{2\pi C} \sqrt{\frac{k}{\mu}}$$

$k$  = stretching force constant of the bond,

$\mu$  = reduced mass of the system defined as

$$\mu = \frac{m_x \cdot m_y}{m_x + m_y}$$

$m_x, m_y$  being the masses of the atoms

X and Y respectively.

#### (B) Polystatomic molecules

For N atomic molecule, '3N' number of coordinates are required to describe all its motions. Since the translational

and rotational motions of the molecule can be described by 3 coordinates each,  $3N-6$  coordinates should describe the vibrations of its atoms and therefore determine the number of vibrational modes ( $3N-5$  for a linear molecule whose rotational motions can be described by two coordinates). In order to describe the vibrational modes of a complex molecule a 'normal mode of vibration' is defined as one in which all the atoms move in phase with the same frequency. The complicated motion of a system of particles can be represented as a superposition of all the normal modes of vibration ( $3N-6$  or  $3N-5$ ). The complex motions of atoms as simplified by the normal vibrations can be determined by classical theory of vibrations. But the procedure requires the knowledge of many force constants which are not easily available and is not practicable especially when the number of atoms in the molecule is large. Hence for the appropriate assignment of the vibrational frequencies, a greatly simplified method based on the observed constancy of bond or group frequencies in different molecules is used. This was first established experimentally and later explained theoretically on the basis of the constancy of bond force constants.

(C) Characteristic group frequencies<sup>19</sup>

The approximate vibrational frequency of a link A-B is determined primarily by the elasticity of the bond, as measured by force constant and by the masses of A and B. If



the force constant between the atoms A and B is the same in one molecule as in another, then they may be expected to give rise to similar vibrational frequencies. And this is indeed observed in many cases where their surroundings are also similar.

An explanation of group frequencies can easily be given in the case of hydrogen stretching vibrations. Since the mass of hydrogen is much smaller than that of the nucleus to which it is usually attached (for example, C, O, N, etc.) the amplitude of vibration of the latter will be much smaller than that of the former. As a first approximation, we may consider the hydrogen nucleus oscillating against an infinitely large mass and therefore the vibrational frequency depends essentially on the force by which hydrogen is bound to that atom in the molecule and will be nearly the same for that group in different molecules (for example, C-H, O-H, N-H have characteristic vibrations).

Apart from the case of the end atoms, bonds involving two atoms will have characteristic frequencies when its force constant is considerably different from those of the surrounding bonds (e.g. multiple bonds between single bonds etc.).

The characteristic frequencies depend on the angle between successive bonds of the atoms in the molecule. If the angle is  $90^\circ$ , there will be no transfer of vibrational energy

from one bond to the next and characteristic frequencies are best defined. However, coupling effects occur when two groups having the same symmetry vibrate with reasonably high and nearly equal frequencies. The C-O stretching and O-H in plane deformation modes of alcohols<sup>19</sup> and carboxylic acids are such cases. In the case of hydrogen modes these can be established by deuteration studies. Thus the compounds containing carboxylic acid groups absorb at  $\sim 1400\text{ cm}^{-1}$  and  $1250\text{ cm}^{-1}$  ascribable to coupled C-O stretching and OH deformation modes. In the deuterated compounds bands at  $\sim 1300\text{ cm}^{-1}$  and  $1050\text{ cm}^{-1}$  are ascribable to C-O stretching and OD deformation modes<sup>20</sup>.

C H A P T E R - I I I

HYDROGEN BONDING



1. Description<sup>21</sup>

Hydrogen bonding occurs when the hydrogen atom of a proton donor group A-H is involved in an inter or intramolecular interaction with a proton acceptor group B. While A is an electronegative atom, such as O, N, F, S, Cl, etc. B is a localised site of high electron density such as a lone pair of electrons of an electronegative atom, a  $\pi$ -electron orbital of a multiple bond etc. H-bonding is a directional and specific interaction which is more localised than weak intermolecular interaction such as repulsion, polarization, dispersion or charge transfer interactions. The strength of H-bonds is small ( $0.5 - 60 \text{ KJ mol.}^{-1}$ ) in comparison with ordinary chemical bonds ( $200-800 \text{ KJ mol.}^{-1}$ ). In hydrogen bonded gases and liquids due to frequent collisions of molecules, H-bonds are continually breaking and reforming resulting in a rapid dynamic equilibrium between the non-bonded and H-bonded species. Thus at ordinary temperature only a fraction of molecules may be in the hydrogen bonded form.

Hydrogen bonds may be intermolecular or intramolecular. When the proton donor and acceptor sites are on the same molecule are such that the angular orientation of the acceptor site does not deviate greatly from the A-H bond axis and is at a distance of  $1.4-2.7 \text{ \AA}$  from the proton, an

intramolecular hydrogen bond may be formed. In intermolecular H-bonding the same above conditions are to be satisfied, but between the proton donor and acceptor sites in two different molecules. Because of its intermolecular nature such hydrogen bonding affects physical properties such as melting and boiling points, heat of vaporization etc. and causes molecular aggregates to be formed.

## 2. Vibrational spectroscopy<sup>22</sup>

Vibrational spectroscopy is one of the most useful techniques for the study of hydrogen bonding behaviour. When H-bonding occurs between a proton donor group A-H and an acceptor group B, a hydrogen bonded complex A-H...B is formed, vibrational frequencies of which are found in the infrared region.

[A] The A-H stretching vibrational frequencies (fundamentals and overtones) are found shifted by ten to several hundred  $\text{cm}^{-1}$  or more from its free A-H value due to a decrease in the force constant on hydrogen bond formation. Further ~~are much~~ *bands* broader (A) than those of the non-hydrogen bonded A-H group (half band width varies from 30  $\text{cm}^{-1}$  to 100  $\text{cm}^{-1}$  or more). The breadth and structure of these bands are however affected very little by change in phase or temperature. In addition to the broadening, the integrated intensity of fundamental A-H stretching bands increases sometimes by factors upto ten or more. However, corresponding overtones decrease slightly in integrated intensity.

These striking intensity effects are probably related to the substantial electrostatic character of the hydrogen bond which may have enhanced the rate of change of the electrostatic dipole moment with internuclear distance.

[B] The A-H deformation modes are shifted to higher frequencies on hydrogen bond formation. These shifts are appreciably smaller than those found for the A-H stretching vibrations. Formation of H-bond constrains the deformation of the A-H bond and therefore increases its force constant. These absorptions do not show any substantial band broadening or intensity change when H-bonding occurs.

[C] New vibrational modes corresponding to H...B stretching and deformation are found at low frequencies (below  $400\text{ cm}^{-1}$ ).

[D] The vibrational modes of acceptor B are shifted by H bonding to higher or lower frequencies and the shifts are generally much smaller than those found for the donor A-H vibrations.

### 3. Weak hydrogen bonds<sup>23,24</sup>

The observed spectral characteristics of the hydrogen bonded compounds tend to indicate essentially two major categories which have been termed weak and strong hydrogen bonds. In the first and the most common category,



the A-H stretching band is found shifted from the free value by a few to as much as  $500\text{ cm}^{-1}$ . The breadth and intensity of the shifted band may have increased by a factor of about 10, ascribed mainly to anharmonicity. The X-ray and neutron diffraction studies show that A-H...B distance in this category is greater than  $2.7\text{ \AA}$  and the hydrogen is located exclusively close to A. In certain cases, the overtone and combination bands of the other internal modes of the A-H...B group like  $\delta_{\text{A-H}}, \nu_{\text{H...B}}$  etc. were found to interact with  $\nu_{\text{A-H}}$  either by Fermi resonance or Stepanov interaction giving rise to various submaxima. Typical of this type are hydroxylic compounds, certain carboxylic acid dimers, amine salts etc. The potential energy curve for such a hydrogen bond may be represented as (A) in Fig. 1.

#### 4. Strong hydrogen bond<sup>25</sup>

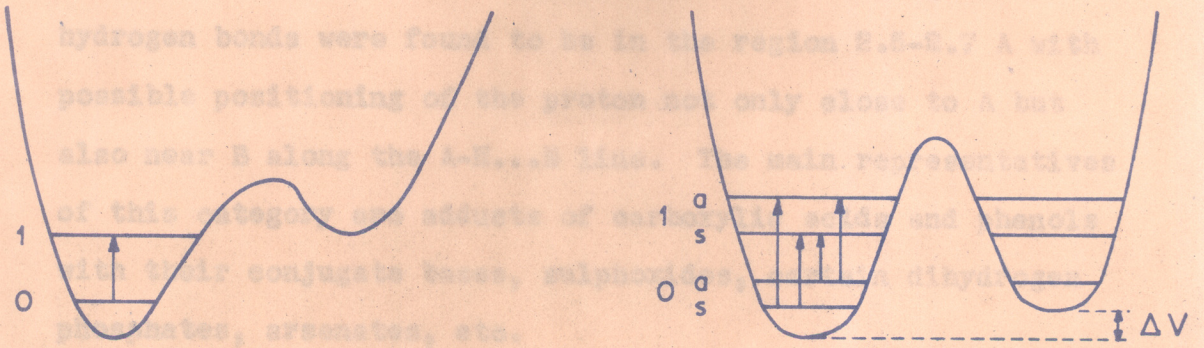
##### [A] Unsymmetrical hydrogen bond

In the second category (strong hydrogen bond) the bands are more complex and there are clearly two types (Hadzi I and II). In the first type the hydrogen atom may occupy either of the two potential minima [Fig. 1, (B) or (C)]. The spectra exhibit generally three regions of A-H stretching absorptions usually at  $2900\text{-}1600\text{ cm}^{-1}$ . They may have smooth contours or may be split into several submaxima. The proton tunnelling in a double minimum potential well is responsible for the unusual spectral characteristics including splitting of vibrational levels. The

TH 239

A

B



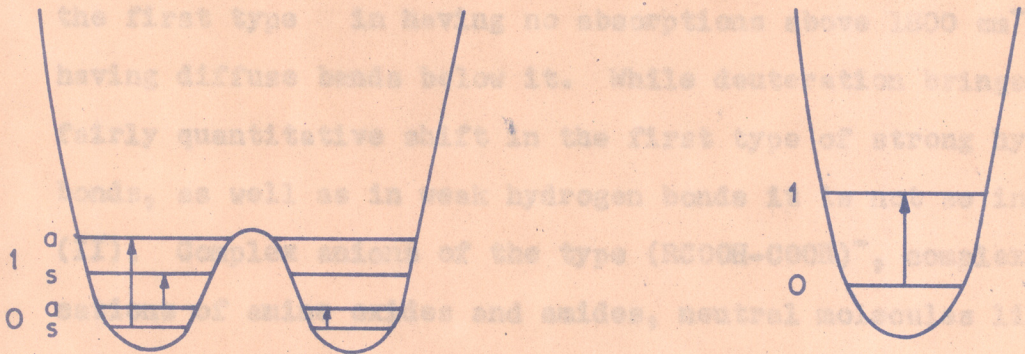
ENERGY ↑

Symmetrical hydrogen bond

In the second type of strong hydrogen bond (label II) hydrogen bond length has decreased below 2.5 Å with the hydrogen placed more or less in the centre of A...B complex. The potential energy of this hydrogen bond may be represented

C

D



$R_A-H \rightarrow$

FIG. 1. POTENTIAL ENERGY DIAGRAM

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A-H...B distances in the solid compounds containing such hydrogen bonds were found to be in the region 2.5-2.7 Å with possible positioning of the proton not only close to A but also near B along the A-H...B line. The main representatives of this category are adducts of carboxylic acids and phenols with their conjugate bases, sulphoxides, certain dihydrogen phosphates, arsenates, etc.

[B]            Symmetrical hydrogen bond

In the second type of strong hydrogen bond (Hadzi II) hydrogen bond length has decreased below 2.5 Å with the hydrogen placed more or less in the centre of A-H...B complex. The potential energy of this hydrogen bond may be represented by Fig. 1(D) and it constitutes nearly symmetrical hydrogen bond. The spectral characteristics are clearly different from the first type in having no absorptions above  $1800\text{ cm}^{-1}$  and having diffuse bands below it. While deuteration brings about fairly quantitative shift in the first type of strong hydrogen bonds, as well as in weak hydrogen bonds it is not so in type (II). Complex anions of the type  $(\text{RCOOH-COOR})^-$ , complex cations of amine oxides and amides, neutral molecules like dimethyl anthranillic acid, p-dichloro diphenyl hydrogen phosphate etc. are typical examples of this type.

CHAPTER IV

EXPERIMENTAL



1. Preparation of compounds and their salts

[A] Mono and dialkyl malonic acids

The preparation of monoalkyl malonic acids has been reported<sup>26</sup>. The dialkyl acids were synthesised following a procedure<sup>27</sup> starting from malonic acid diethyl ester, treating with sodium and corresponding alkyl iodide to obtain the dialkyl derivative and alkaline hydrolysis to obtain the acids. To obtain pure diethyl malonic acid m. p. 125° and di-n-propyl malonic acid m. p. 161° they were crystallized twice from toluene and chloroform respectively.

[B] Tetraalkyl succinic acids

The tetramethyl succinic acid was prepared following the reported procedure<sup>28</sup> starting from hydrazine dichloride, sodium cyanide and dimethyl ketone to obtain hydrazodinitrile. The latter was oxidised to the azodinitrile which on acid hydrolysis gave the corresponding tetramethyl succinic acid. It was recrystallized from chloroform to obtain a product with m. p. 200°C.

When tetra n-propyl succinic acid was prepared on similar lines the yield was very poor. The above procedure was therefore modified. The azodinitrile was converted to dinitrile by heating it in a sealed tube in oil bath at 120° for one hour. The dinitrile was then heated with 80% H<sub>2</sub>SO<sub>4</sub> at 120° for one

hour to obtain anhydride which on refluxing with 1M aqueous KOH for four hours gave the acid. It was recrystallized from  $\text{CHCl}_3$  to obtain a product with m. p.  $137^\circ\text{C}$ .

[C] Monoalkali salts

These were prepared by adding one equivalent of alkaline hydroxide or carbonate solution under stirring to the aqueous solution of the acid and subsequent evaporation of water and drying at  $110^\circ$  under vacuum. The melting points and microanalyses results are tabulated in Table I.

[D] Deuterated derivatives

Deuteration of the acids and salts was carried out by refluxing with 99.8%  $\text{D}_2\text{O}$  (supplied by Atomic Energy Establishment, Bombay) for half an hour and distilling off the  $\text{D}_2\text{O}$ . The samples were then dried as before.

2. Instrumental

The spectra were recorded on a Perkin-Elmer 221 Infrared Spectrophotometer equipped with a sodium chloride-grating interchange. The instrument was calibrated with carbon dioxide and water vapour bands and checked with polystyrene before recording each spectrum. Spectra were taken in Nujol ( $1800\text{-}1500$ ,  $1300\text{-}600\text{ cm}^{-1}$ ) and hexachlorobutadiene ( $3700\text{-}1800$ ,  $1500\text{-}1300\text{ cm}^{-1}$ ) mulls. Solution spectra in dimethyl sulphoxide (spectrophotometric grade distilled)

T A B L E - I

Melting points and Microanalysis  
results

Compound	Molecular formula	Melting point <sup>°C</sup> (Uncorr.)	% carbon		% hydrogen	
			Found	Calc.	Found	Calc.
Ethyl malonic acid	$C_5H_8O_4$	111.5	45.4	45.4	6.16	6.00
n-Pentyl malonic acid	$C_8H_{14}O_4$	82	54.5	55.2	7.98	8.00
Dimethyl malonic acid	$C_5H_8O_4$	192	45.1	45.4	6.14	6.00
Diethyl malonic acid	$C_7H_{12}O_4$	125	52.2	52.5	7.82	7.50
Di-n-propyl malonic acid	$C_9H_{16}O_4$	161	56.4	57.4	8.47	8.50
Ethyl malonic acid mono k salt	$C_5H_7O_4k$		36.2	35.3	5.31	4.10
n-Pentyl malonic acid mono Na salt	$C_8H_{13}O_4Na$		49.3	49.0	6.30	6.60
Dimethyl malonic acid mono k salt	$C_5H_7O_4k$		34.6	35.3	4.65	4.10
Diethyl malonic acid mono k salt	$C_7H_{11}O_4k$		43.2	42.4	5.13	5.55
Di-n-propyl malonic acid mono k salt	$C_9H_{15}O_4k$		47.8	47.8	5.82	6.60

Table 1 .. continued...

Tetramethyl succinic acid	$C_8H_{14}O_4$	200	54.9	55.1	8.05	8.04
Tetra-n-propyl succinic acid anhydride	$C_{16}H_{28}O_3$	78	72.1	71.6	10.79	10.45
Tetramethyl succinic acid mono Na salt	$C_8H_{13}O_4Na$		49.6	49.0	6.43	6.70
Tetra-n-propyl succinic acid mono Na salt	$C_{16}H_{29}O_4Na$		62.4	62.3	9.50	9.40
Malonic acid mono Li salt	$C_3H_3O_4Li$		32.4	32.7	2.76	2.72
Malonic acid mono Na salt	$C_3H_3O_4Na$		28.6	28.6	2.33	2.37
Malonic acid mono k salt	$C_3H_3O_4k$		25.6	25.3	2.77	2.10
Malonic acid mono Rb salt	$C_3H_3O_4Rb$		19.0	19.1	1.59	1.75
Malonic acid mono Cs salt	$C_3H_3O_4Cs$		16.5	15.3	1.40	1.27

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dried over calcium hydride immediately before use, were taken in 0.1 mm path length cell filled in dry box with solvent compensation. The proton magnetic resonance spectra were recorded on a Varian T-60 instrument with TMS as internal standard using the above DMSO as solvent.



CHAPTER - V

RESULTS AND DISCUSSION

MONOALKALI SALTS OF ALKYL MALONIC AND SUCCINIC  
ACIDS

Monoalkali salts of alkyl malonic and succinic acids

1. Monoalkali salts of monoalkyl malonic acids

The infrared spectra of both solid mono-sodium and mono-potassium salts of monoethyl and mono *n*-pentyl malonic acids (Fig. 2 and 3, Table II) were similar, unlike those of the mono-sodium and mono-potassium salts of malonic acid (see later). They were comparable to the spectrum of sodium hydrogen malonate and showed medium strong and broad absorption at 2500 and 1900  $\text{cm}^{-1}$  in place of the broad absorptions at 3000 and 2700  $\text{cm}^{-1}$  found in the parent acids. On deuteration the band at 2500  $\text{cm}^{-1}$  disappeared but the shifting of 1900  $\text{cm}^{-1}$  could not be ascertained due to overlapping with the band shifted from 2500  $\text{cm}^{-1}$  and strong absorptions at 1300  $\text{cm}^{-1}$ . The carboxylic (C=O) and the carboxylate ( $\text{COO}^-$ ) stretching modes were found in the usual regions at 1710 - 1680 and 1580  $\text{cm}^{-1}$  respectively. The other carboxylic ( $\nu_{\text{C-O}} + \delta_{\text{OH}}$ ) and carboxylate (symmetric stretching) absorptions were found at 1370-1360, 1280 and 1320-1310  $\text{cm}^{-1}$  respectively. The hydroxyl bands at 2500 and 1900  $\text{cm}^{-1}$  and normal carboxylic and carboxylate absorptions are characteristic of strongly hydrogen bonded system involving a double minimum potential type of hydrogen bond (Hadzi type I)<sup>25</sup>. To decide whether the hydrogen bonding is intermolecular or intramolecular in nature, the spectra were recorded in dimethyl sulphoxide. The infrared spectra in DMSO solution were similar to those of the solid in

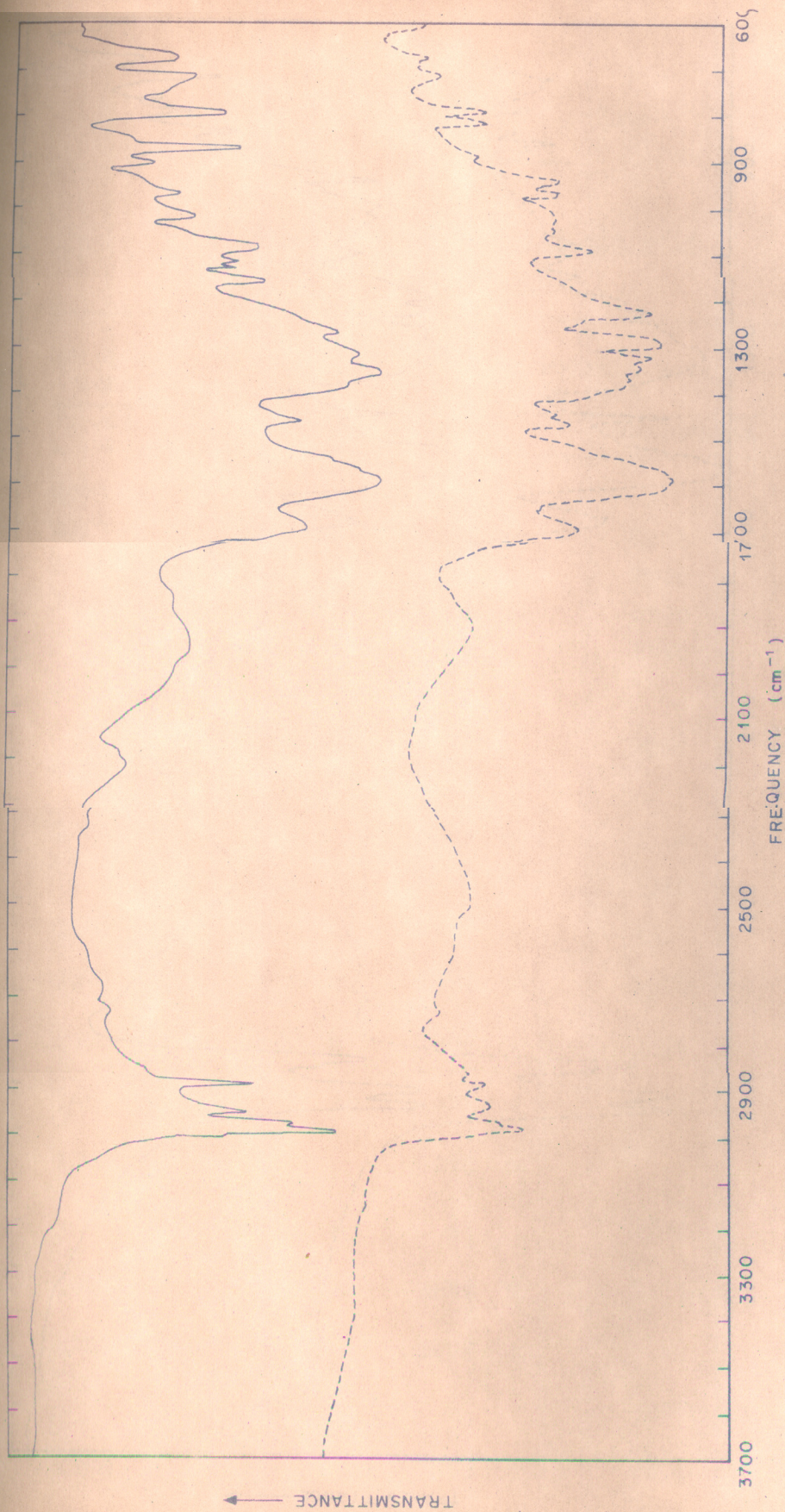


FIG. 2. IR SPECTRA OF ETHYL MALONIC ACID MONO Na SALT (-----),  
 DEUTERATED ANALOGUE (—————)



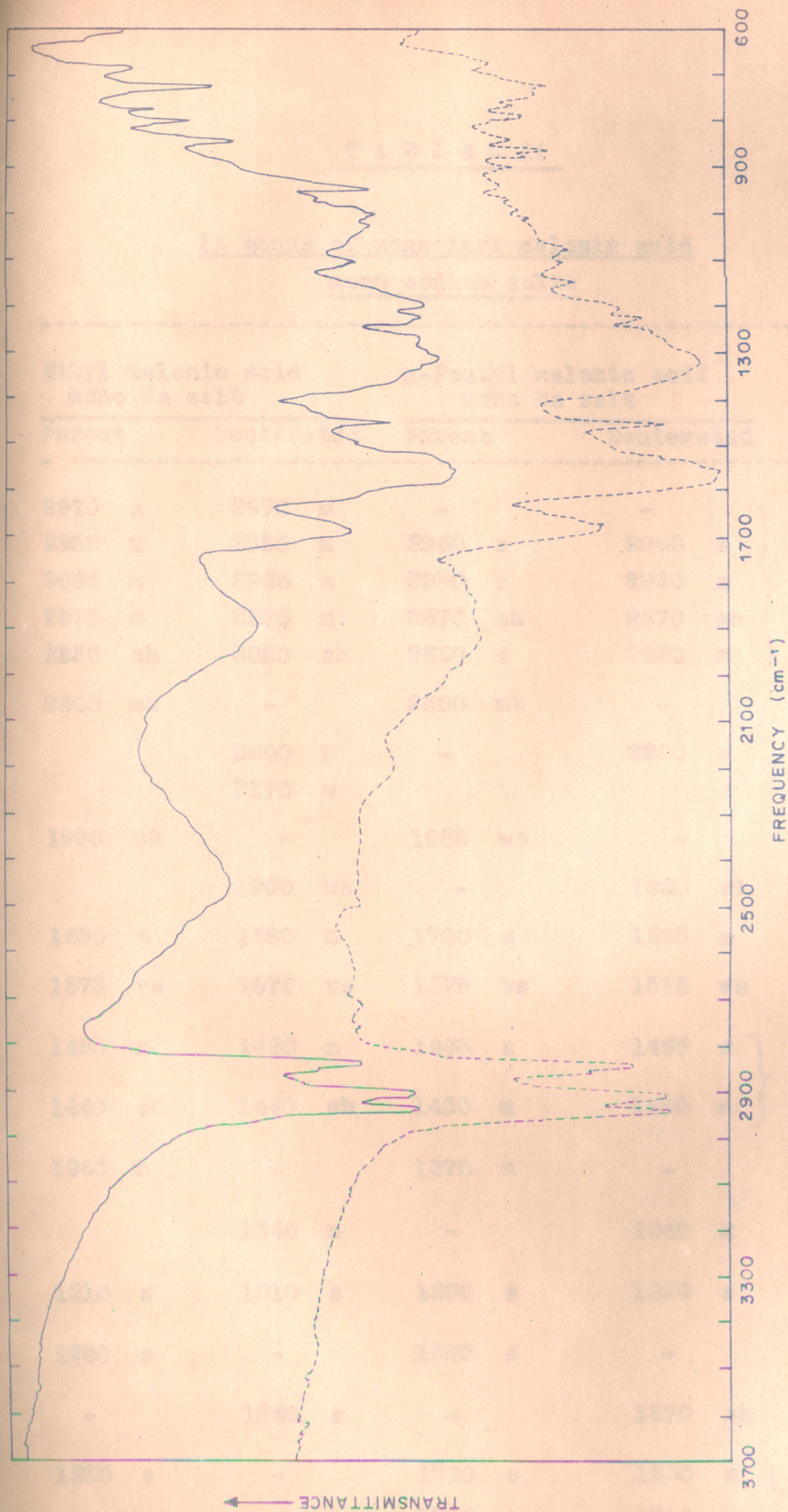


FIG. 3. IR SPECTRA OF n-PENTYL MALONIC ACID MONO Na SALT (————),  
DEUTERATED ANALOGUE (-----)

T A B L E - II

IR bands of monoalkyl malonic acid  
mono sodium salts

Ethyl malonic acid mono Na salt		n-Pentyl malonic acid mono Na salt		Assignment
Parent	Deuterated	Parent	Deuterated	
2970 s	2970 m	-	-	} $\nu$ CH, CH <sub>2</sub> , CH <sub>3</sub>
2955 m	2955 m	2960 s	2960 s	
2935 m	2935 m	2920 s	2920 s	
2875 m	2875 m	2870 sh	2870 sh	
2850 sh	2850 sh	2860 s	2860 s	
2500 mb	-	2500 mb	-	$\nu$ OH
	2200 w	-	2200 w	$\nu$ CD
	2170 w			
1950 wb	-	1950 wb	-	$\nu$ OH
	1950 wb	-	1920 wb	$\nu$ OD
1690 m	1690 m	1700 m	1685 m	$\nu$ C=O
1575 vs	1575 vs	1575 vs	1575 vs	$\nu$ COO <sup>-</sup> asym.
1460 m	1460 m	1465 s	1465 s	} $\delta$ CH <sub>2</sub> , CH <sub>3</sub> .
1440 sh	1440 sh	1450 m	1450 m	
1360 m	-	1370 m	-	( $\nu$ CO + $\delta$ OH)
	1340 m	-	1340 m	( $\nu$ CO + $\delta$ OD)
1310 s	1310 s	1320 s	1320 s	$\nu$ COO <sup>-</sup> sym.
1280 s	-	1280 s	-	( $\nu$ CO + $\delta$ OH)
-	1260 s	-	1270 sh	( $\nu$ CO + $\delta$ OD)
1220 s	-	1230 s	1230 s	} CH <sub>2</sub> wag.
		1210 s	1210 m	



Table II ... continued.

	1150 m	-	1160 m	} $\int$ CD <sub>2</sub>
	1120 w	-	-	
	1110 w	-	1110 w	
1080 m	1080 m	1110 m	-	CH <sub>2</sub> twist.
	1010 m	-	1080 sh	CD <sub>2</sub> wag.
960 m	960 m	-	-	$\vee$ C-C
1010 mb	-	1030 w	} $\int$ OH(o.p.p.)	
940 m	-	1010 w		
		975 w		
		950 w		
	900 m		} $\int$ CD <sub>2</sub> twist.	
	860 m	860 m		
810 m	-	840 m	} $\int$ CH <sub>2</sub> rock.	
		800 w		
790 m	790 m		$\int$ COO <sup>-</sup>	
	740 sh	-	} $\int$ OD	
	720 m			
		720 m	$\int$ COO <sup>-</sup>	
670 m	-	685 m	685 sh	$\int$ COOH

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the region  $2700-1500\text{ cm}^{-1}$ . This behaviour is similar to that of the monosodium salt of malonic acid. The PMR spectrum of *n*-pentyl malonic acid monosodium salt in DMSO showed a concentration dependence for the carboxylic OH (440-378 cps with respect to tetra methyl silane (TMS) in the concentration range of 2-1%). The above spectral results show that the double minimum potential type hydrogen bonding in monosodium salts of monoalkyl malonic acids is intermolecular in nature in dimethyl sulphoxide. The intermolecular hydrogen bonding between the carboxylic proton and carboxylate ion in the solid state is replaced by intramolecular hydrogen bonding between the carboxylic OH and DMSO. Thus the monoalkyl substitution of malonic acid does not change the hydrogen bonding behaviour of their monosodium salts just as the ratio of the dissociation constants  $k_1/k_2$  in water.

## 2. Monoskali salts of dialkyl malonic acids

The infrared spectra of dimethyl, diethyl and di-*n*-propyl malonic acid monopotassium salts are given in Fig. 4 (Table III, IV). It can be seen that the spectra of diethyl and di-*n*-propyl malonic acid monopotassium salt are quite different from that of dimethyl malonic acid monopotassium salt which resembles the spectrum of parent malonic acid monosodium salt in the region  $3700-1500\text{ cm}^{-1}$ . The spectrum of dimethyl malonic acid monopotassium salt shows carboxylic and carboxylate

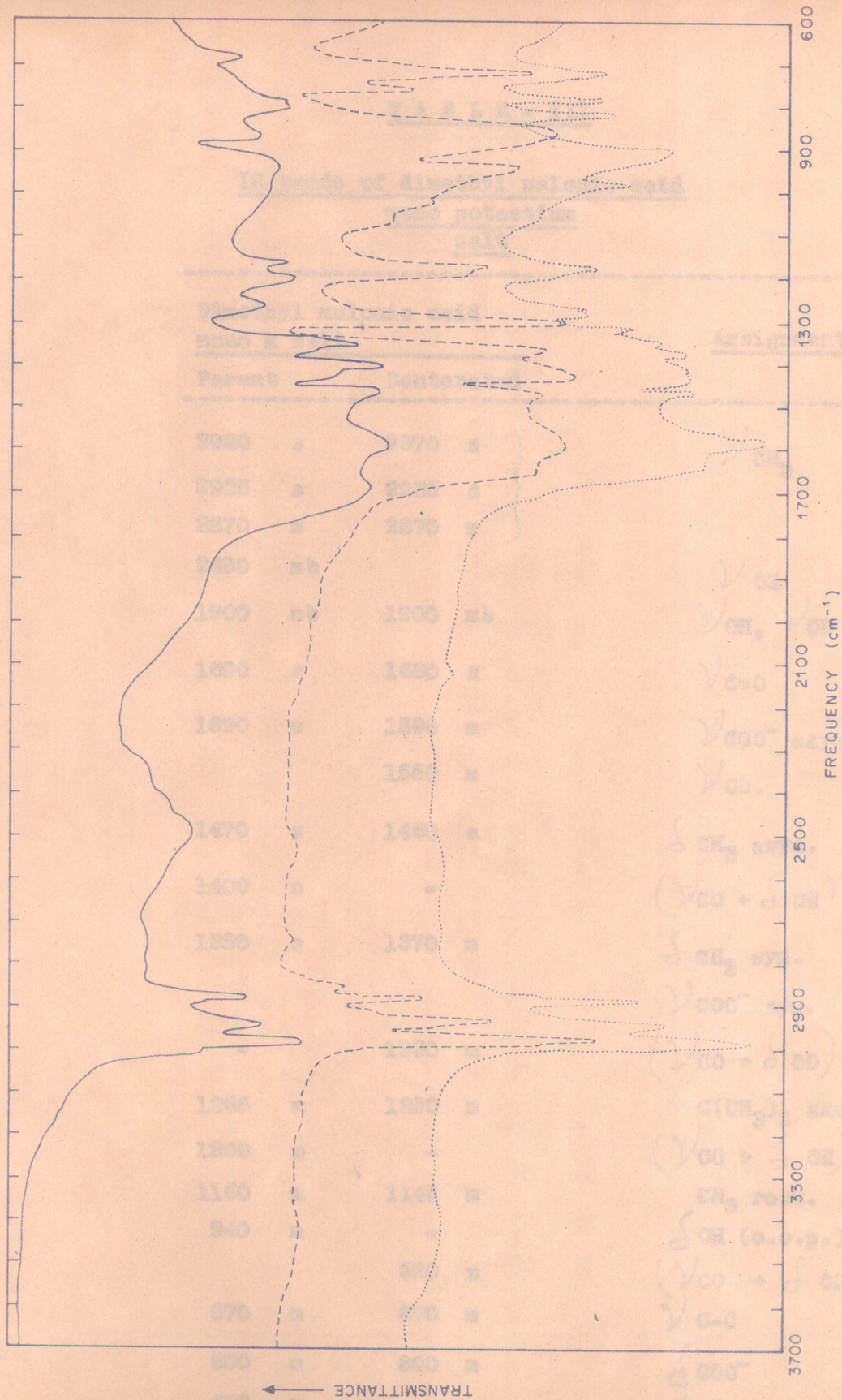


FIG. 4. IR SPECTRA OF DIMETHYL MALONIC ACID MONO K SALT (———),  
DIETHYL MALONIC ACID MONO K SALT (-----),  
Di-n-PROPYL MALONIC ACID MONO K SALT (.....)

TABLE - III

IR bands of dimethyl malonic acid  
mono potassium  
salt

Dimethyl malonic acid mono k salt				<u>Assignments</u>
Parent		Deuterated		
2980	s	2970	s	} $\nu$ CH <sub>3</sub>
2935	s	2935	s	
2870	m	2870	m	
2490	mb			$\nu$ OH
1900	mb	1900	mb	$\nu$ OH, $\nu$ OD
1690	s	1680	s	$\nu$ C=O
1590	s	1590	m	$\nu$ COO <sup>-</sup> asym.
		1550	m	$\nu$ OD.
1470	s	1460	s	$\delta$ CH <sub>3</sub> asym.
1400	s	-		( $\nu$ CO + $\delta$ OH)
1350	s	1370	m	$\delta$ CH <sub>3</sub> sym.
				$\nu$ COO <sup>-</sup> sym.
-		1330	m	( $\nu$ CO + $\delta$ OD)
1265	m	1250	m	C(CH <sub>3</sub> ) <sub>2</sub> skeletal.
1200	m	-		( $\nu$ CO + $\delta$ OH)
1160	m	1145	m	CH <sub>3</sub> rock.
940	m	-		$\delta$ OH (o.o.p.)
		920	m	( $\nu$ CO + $\delta$ OD)
870	m	860	m	$\nu$ C-C
800	m	800	m	$\delta$ COO <sup>-</sup>
680	m	-		$\delta$ COOH



T A B L E - I V

IR bands of dialkyl malonic acid mono  
potassium salts

Diethyl malonic acid mono k salt	Di-n-propyl malonic acid mono k salt	Assignments
2970 s	2960 s	} $\nu_{\text{CH}_3, \text{CH}_2}$
2930 s	2930 s	
2880 m	2870 s	
2850 w		
1650 mb	1630 mb	$\nu_{\text{C=O}}$
1590 s	1580 s	$\nu_{\text{COO}^-}, \delta_{\text{OH}}$
1470 s	1460 s	} $\delta_{\text{CH}_3}, \delta_{\text{CH}_2}$
1430 s	1430 sb	
1370 s	1370 s	$\delta_{\text{CH}_3 \text{ sym.}}$
1305 s	1340 m	} $\text{CH}_2 \text{ wag.}$
	1310 m	
	1290 m	
	1260 m	
1190 sh	1180 sb	} $\text{CH}_2 \text{ twist}$
1175 s		
1070 sh	1030 w	} $\nu_{\text{C-C}}$
1035 w	1010 w	
950 s, b	980 sb	} $\nu_{\text{OH}}$
860 s, b	900 sb	
760 m	810 s	} $\text{CH}_2 \text{ rock.}$
720 s	775 s	
	720 s	



absorptions in the characteristic regions of  $\sim 1700$  and  $\sim 1580 \text{ cm}^{-1}$  respectively and broad absorptions at  $2500$  and  $1900 \text{ cm}^{-1}$  ascribable to hydroxyl stretching vibrations of a double minimum potential type hydrogen bond. The inter or intramolecular nature of the hydrogen bonding in the potassium salt of dimethyl malonic acid could not be decided since no hydroxyl proton signal could be located in PMR spectrum in DMSO even after repeated trials. However, the infrared spectrum in DMSO showed little change from that of the solid.

The infrared spectra of diethyl and di-n-propyl malonic acid monopotassium salts are characterised by absorption bands in the region  $1650-1500 \text{ cm}^{-1}$  which consisted of two broad bands ascribed to a considerably perturbed C=O of the carboxylic group at  $1650-1630 \text{ cm}^{-1}$ . Another set of bands appeared in the region  $1100-800 \text{ cm}^{-1}$  which consisted of atleast two strong broad bands lying between  $980-860 \text{ cm}^{-1}$  and weaker bands between  $1100-1000 \text{ cm}^{-1}$ . The absence of any band ascribable to a hydroxyl absorption in the region above  $1650 \text{ cm}^{-1}$ , appreciable shift in the carboxyl absorption and strong absorption in the region  $1100-800 \text{ cm}^{-1}$  are characteristics of strongly hydrogen bonded systems which approached a symmetrical hydrogen bond (Hadzi type II)<sup>25</sup>. The spectra in the entire region remained unchanged on deuteration except for some small changes in the intensities of bands at  $1650-1500 \text{ cm}^{-1}$  and  $1000-800 \text{ cm}^{-1}$  which may be ascribed to  $\delta_{\text{OH}}$  and  $\nu_{\text{OH}}$  modes respectively. While the shifted bands corresponding to those at

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1650-1500  $\text{cm}^{-1}$  could not be located, those due to 1000-800  $\text{cm}^{-1}$  were located at 640-610  $\text{cm}^{-1}$  in the deuterated di-n-propyl derivative. In potassium hydrogen succinate bands at 1540 and 850  $\text{cm}^{-1}$  have been assigned<sup>29</sup> to  $\int_{\text{OH}}$  and  $\int_{\text{OH}}$  respectively. The splitting of the bands at 800 into 810 and 770  $\text{cm}^{-1}$  in potassium salt of di-n-propyl malonic acid suggests more than one rotational conformation for the alkyl group.

In order to get more information on the diethyl and di-n-propyl malonic acid potassium salts the infrared spectra were recorded in DMSO in the region 2700-1500  $\text{cm}^{-1}$ . There was no difference in the band position compared to those of the solid spectra even after five fold dilution (2.5-0.5%). This indicates that symmetrical hydrogen bond in the solid is unaffected in DMSO and therefore, must be intramolecular in nature. Strong support for this conclusion was found in a PMR study of the monopotassium salt of diethyl malonic acid in DMSO (Fig.5). The carboxylic proton showed a chemical shift of 1180 cps with respect to TMS which was independent of concentration in the range 3-1%. Proton resonance shifts of 924, 901 and 909 cps with respect to water have been reported<sup>30</sup> for symmetric intramolecular hydrogen bonds in potassium and sodium hydrogen maleates and potassium hydrogen phthalate respectively in DMSO. These results suggest that there is a strong intramolecular hydrogen bonding which is nearly symmetrical in the solid and in DMSO solution. This is in contrast to the weaker double minimum

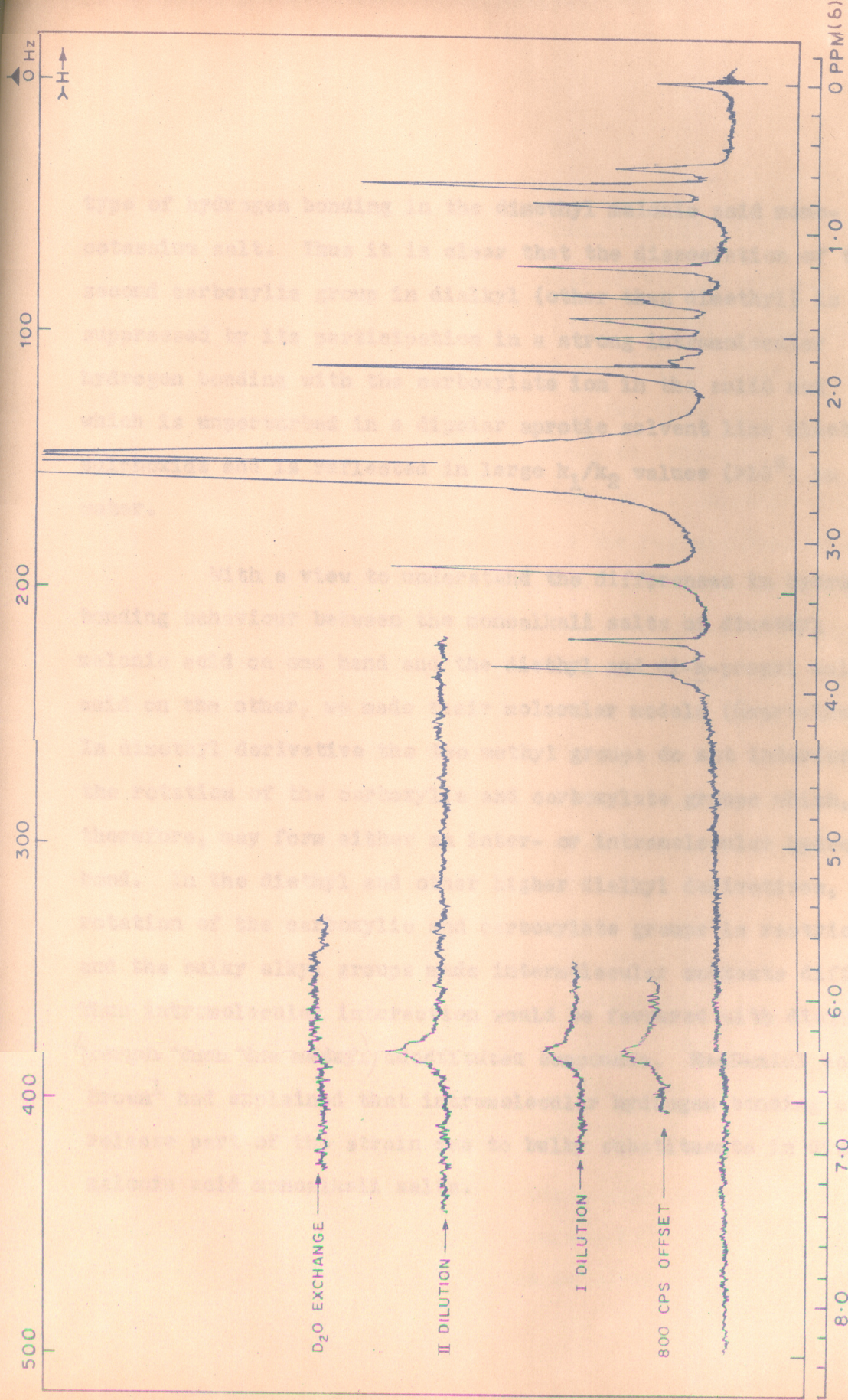


FIG. 5. PMR SPECTRUM OF DIETHYL MALONIC ACID MONO K SALT



type of hydrogen bonding in the dimethyl malonic acid mono-potassium salt. Thus it is clear that the dissociation of the second carboxylic group in dialkyl (other than dimethyl) is suppressed by its participation in a strong intramolecular hydrogen bonding with the carboxylate ion in the solid and which is unperturbed in a dipolar aprotic solvent like dimethyl sulphoxide and is reflected in large  $k_1/k_2$  values ( $>10^4$ ) in water.

With a view to understand the differences in hydrogen bonding behaviour between the monoalkali salts of dimethyl malonic acid on one hand and the diethyl and di-n-propyl malonic acid on the other, we made their molecular models (Courtalds). In dimethyl derivative the two methyl groups do not interfere in the rotation of the carboxylic and carboxylate groups which, therefore, may form either an inter- or intramolecular hydrogen bond. In the diethyl and other higher dialkyl derivatives, the rotation of the carboxylic and carboxylate groups is restricted and the bulky alkyl groups made intermolecular contacts difficult. Thus intramolecular interaction would be favoured with dialkyl (larger than the methyl) substituted compounds. MacDaniel and Brown<sup>1</sup> had explained that intramolecular hydrogen bonding could release part of the strain due to bulky substituents in dialkyl malonic acid monoalkali salts.

### 3. Monoalkali salts of tetraalkyl succinic acids

The spectra of monosodium salt of tetramethyl and tetra-*n*-propyl succinic acids (Fig. 6, Table V) were found to be similar. The spectra showed strong absorption bands in the region 1700-1550  $\text{cm}^{-1}$  which consisted of two broad bands ascribable to C=O of the carboxylic group at 1700-1620  $\text{cm}^{-1}$  and a carboxylate absorption at 1570-1550  $\text{cm}^{-1}$ . Another set of strong absorption bands was found in the region 1200-800  $\text{cm}^{-1}$ . The spectra showed very little change on deuteration except some changes in the positions and intensities of bands at 1660-1500  $\text{cm}^{-1}$  and 1000-800  $\text{cm}^{-1}$  which may be ascribed to  $\delta_{\text{OH}}$  and  $\nu_{\text{OH}}$  respectively. The absence of hydroxyl band in the region above 1700  $\text{cm}^{-1}$ , absorption at 1660-1500  $\text{cm}^{-1}$  and 1000-800  $\text{cm}^{-1}$  which are affected very little on deuteration are characteristic of strongly hydrogen bonded systems, which approached a symmetrical hydrogen bond (Hadzi type II).

The PMR spectrum of tetramethyl succinic acid monosodium salt (Fig. 7) showed that the chemical shift due to hydroxyl proton was at 1160 cps with respect to TMS and was independent of concentration in the range of 1-0.5%. This confirmed the earlier conclusion of a nearly symmetrical intramolecular hydrogen bond.

In the tetra-*n*-propyl succinic acid monosodium salt the chemical shift of the hydroxyl proton was 1170 cps. Due to poor solubility the concentration dependence of chemical shift could not be determined.



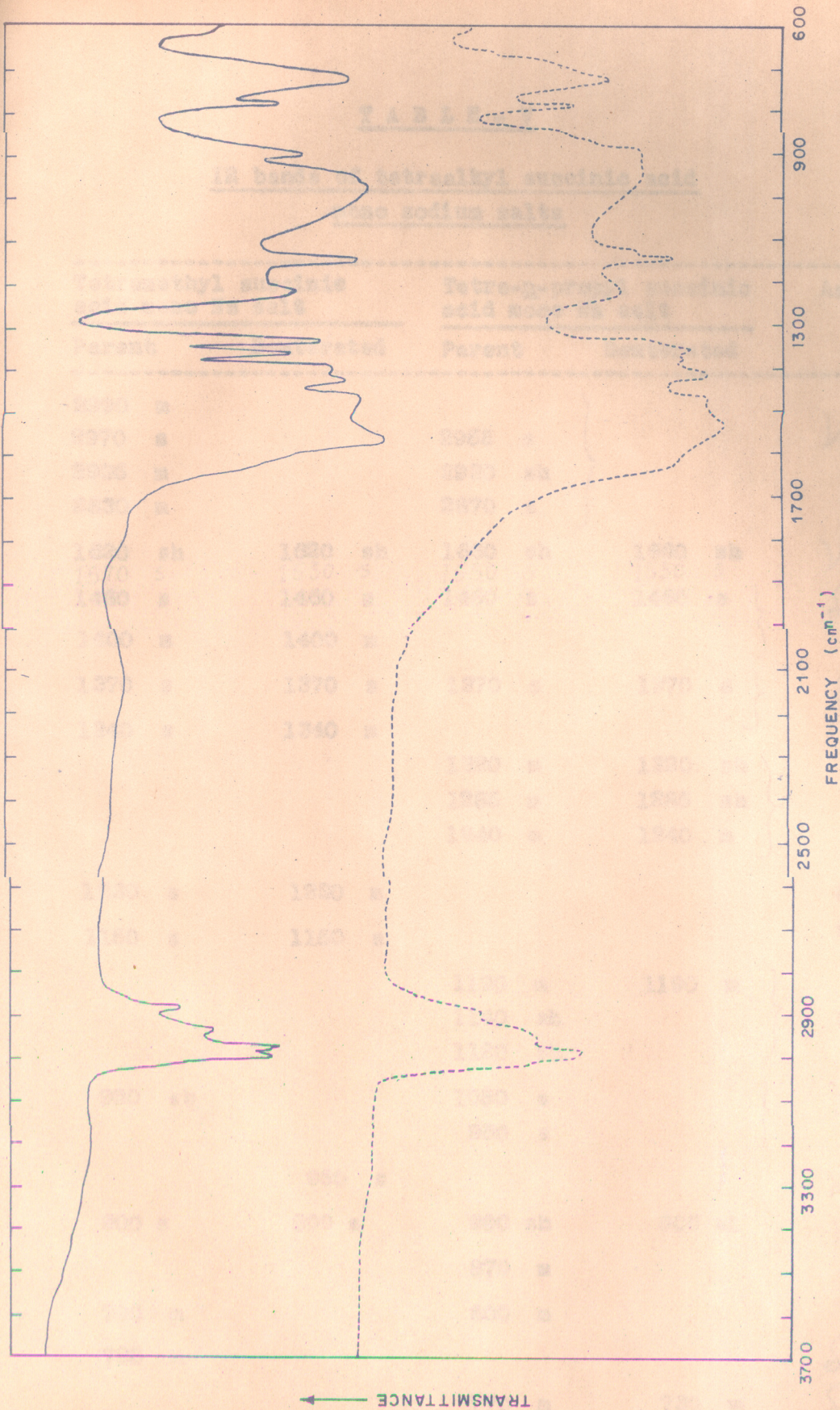


FIG. 6. IR SPECTRA OF TETRAMETHYL SUCCINIC ACID MONO Na SALT (——),  
 DEUTERATED ANALOGUE (-----)

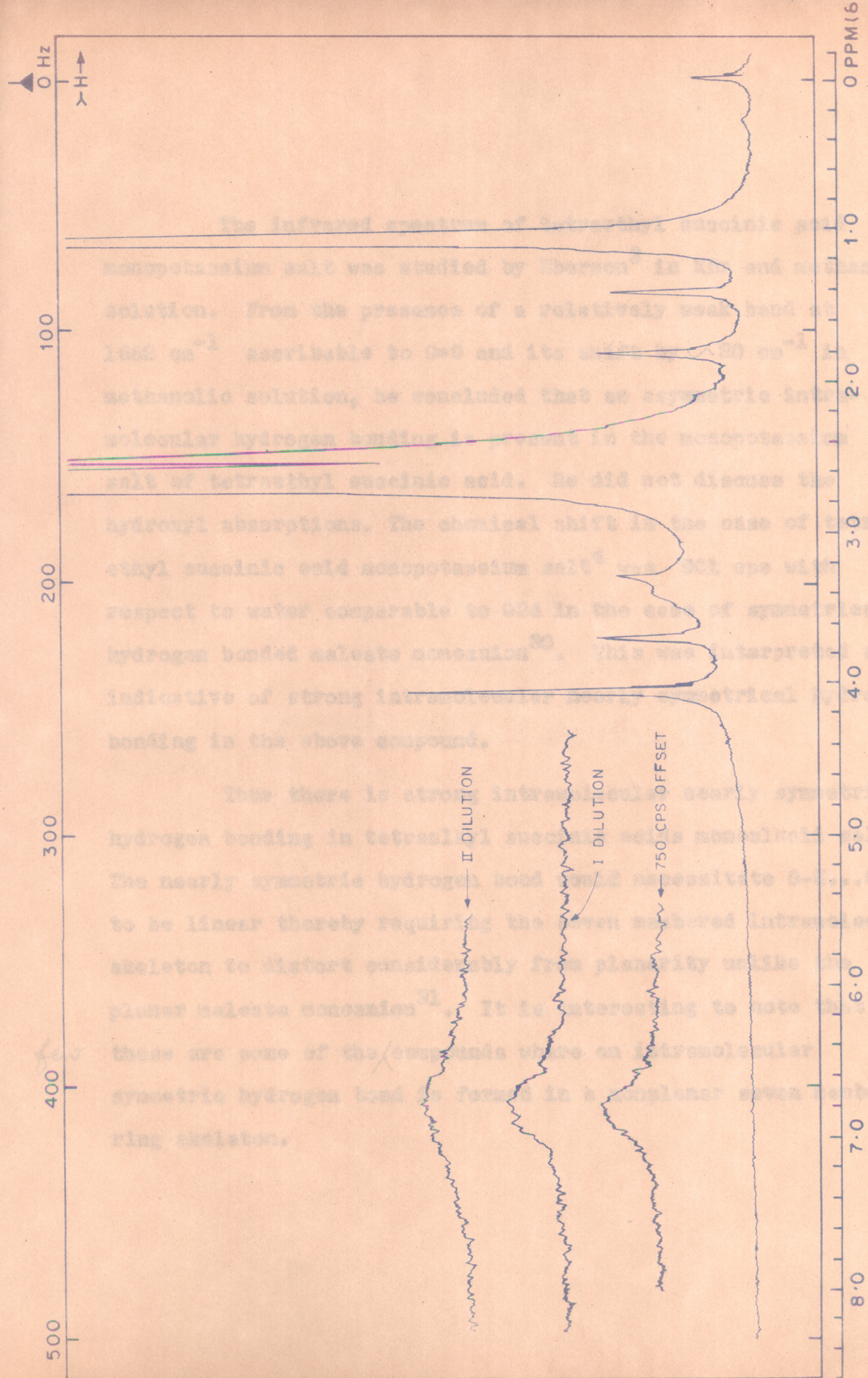
TABLE - V

IR bands of tetraalkyl succinic acid  
mono sodium salts

Tetramethyl succinic acid mono Na salt		Tetra-n-propyl succinic acid mono Na salt		Assignment
Parent	Deuterated	Parent	Deuterated	
2990	m			} $\nu_{\text{CH}_3, \text{CH}_2}$
2970	s	2955	s	
2935	m	2930	sh	
2830	m	2870	s	
1620	sh	1620	sh	} $\nu_{\text{C=O}}$ $\nu_{\text{COO}^-}$ $\delta_{\text{OH}}$ $\delta_{\text{CH}_3}$ <i>asym.</i>
1570	s	1530	s	
1460	s	1460	s	
		1460	s	
1400	m	1400	m	} $\delta_{\text{CH}_3}$ sym.
1370	s	1370	s	
1340	s	1340	m	
		1320	m	} $\text{CH}_2$ wag.
		1285	m	
		1240	m	
1230	s	1230	m	} $\text{C}(\text{CH}_3)_2$ skeletal.
1150	s	1150	s	
		1190	m	} $\text{CH}_2$ twist.
		1140	sh	
		1120	sh	
990	sb	1050	s	} $\nu_{\text{OH}}$
		950	s	
		950	s	} $\nu_{\text{OD}}$
900	s	900	s	
		900	sh	} $\nu_{\text{C-C}}$ $\text{CH}_2$ rock.
		870	m	
790	m	800	m	} $\text{CH}_3$ rock.
720	m			
		770	m	} $\delta_{\text{C-C-C}}$
		730	m	
				} $\delta_{\text{COO}^-}$



FIG. 7. PMR SPECTRUM OF TETRAMETHYL SUCCINIC ACID MONO Na SALT



The infrared spectrum of tetraethyl succinic acid monopotassium salt was studied by Ebersson<sup>3</sup> in KBr and methanol solution. From the presence of a relatively weak band at  $1682\text{ cm}^{-1}$  ascribable to C=O and its shift by  $\sim 20\text{ cm}^{-1}$  in methanolic solution, he concluded that an asymmetric intramolecular hydrogen bonding is present in the monopotassium salt of tetraethyl succinic acid. He did not discuss the hydroxyl absorptions. The chemical shift in the case of tetraethyl succinic acid monopotassium salt<sup>4</sup> was 901 cps with respect to water comparable to 924 in the case of symmetrically hydrogen bonded maleate monoanion<sup>30</sup>. This was interpreted as indicative of strong intramolecular nearly symmetrical hydrogen bonding in the above compound.

Thus there is strong intramolecular nearly symmetric hydrogen bonding in tetraalkyl succinic acids monoalkali salts. The nearly symmetric hydrogen bond would necessitate O-H...O to be linear thereby requiring the seven membered intramolecular skeleton to distort considerably from planarity unlike the planar maleate monoanion<sup>31</sup>. It is interesting to note that *few* these are some of the ~~compounds~~ where an intramolecular symmetric hydrogen bond is formed in a nonplanar seven membered ring skeleton.

CHAPTER - VI

RESULTS AND DISCUSSIONS

MONOALKALI SALTS OF MALONIC ACID



### Monoalkali Salts of Malonic Acid

The infrared spectra of mono Li and Na salts of malonic acid are shown in Fig. 8 (Table VI). The spectrum of mono Li salt was found to be comparable with the spectrum of mono Na salt. The spectra of these salts show a very broad band at  $\sim 2500 \text{ cm}^{-1}$  and two medium bands at  $2780$  and  $1900 \text{ cm}^{-1}$  and strong absorptions at  $1740$ ,  $1680$  and  $1585$  with well defined bands in the lower frequency region. The above pattern especially bands at  $2780$ ,  $2500$  and  $1900 \text{ cm}^{-1}$  is characteristic of an unsymmetrical hydrogen bond of a double minimum potential type (Hadzi I). Deuteration had confirmed the above conclusion in the case of mono sodium salt<sup>16</sup>. In order to establish the nature of species in solution the spectra were recorded in DMSO. The nearly similar IR spectrum and the concentration dependence of the PMR spectrum (NaH malonate 500-400 cps with respect to TMS at 60 M. cps in the concentration range of 1-0.3%) suggested the existence of an intermolecular unsymmetrical hydrogen bonding in DMSO solution.

The infrared spectra of mono K, Rb and Cs salts are given in Fig. 9 (Table VII). These spectra are considerably different from the spectra of mono Li and Na salts. There are no bands in the region  $2800-1800 \text{ cm}^{-1}$  but a strong band at  $\sim 1700 \text{ cm}^{-1}$  with diffuse broad absorptions in the low frequency region ( $1200 - 800 \text{ cm}^{-1}$ ) is found in these salts. There was little change on deuteration. These features are characteristic of a nearly

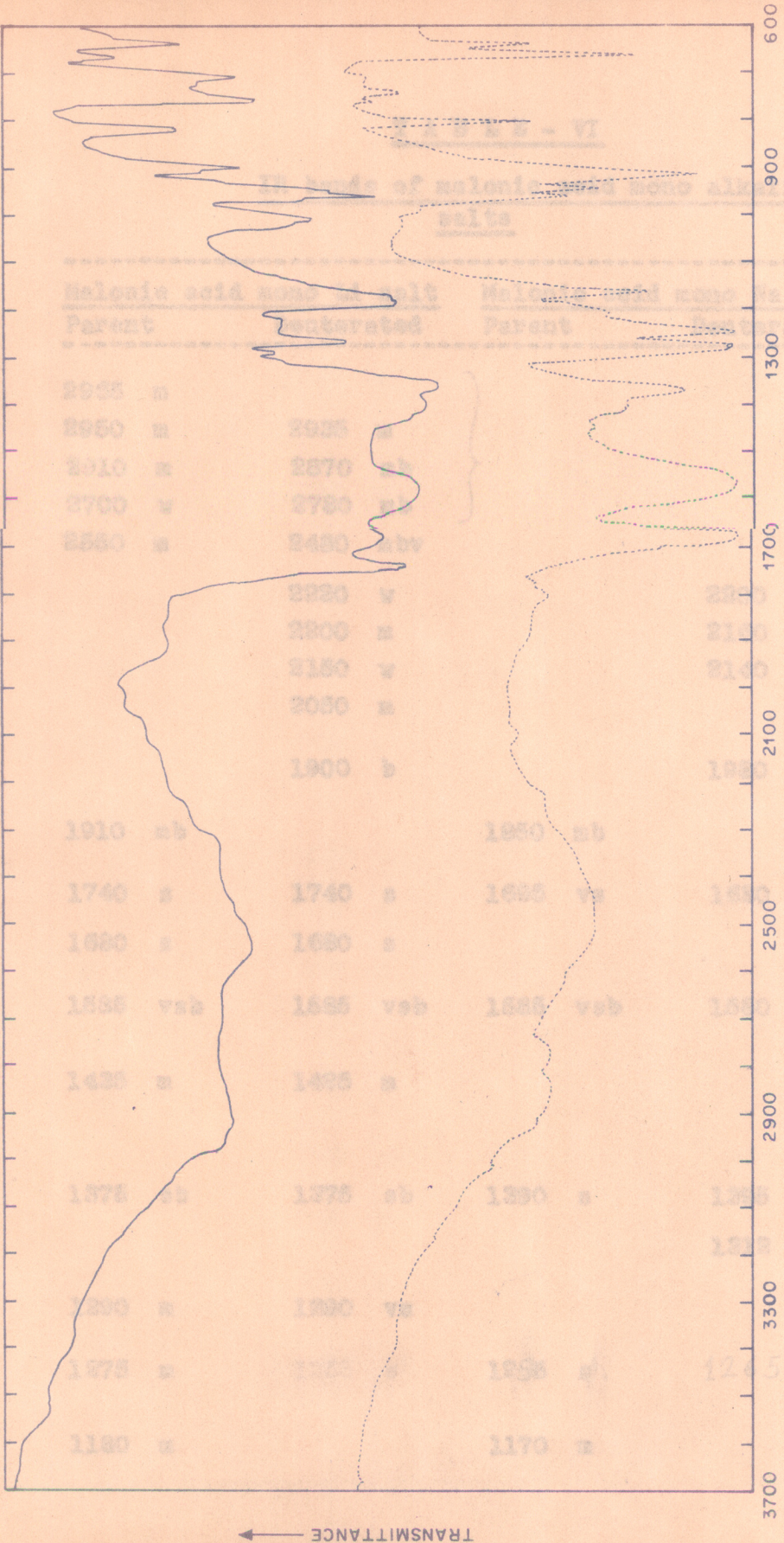


FIG. 8. IR SPECTRA OF MALONIC ACID MONO LI SALT ( ——— ),  
MONO Na SALT ( ..... )

T A B L E - VI

IR bands of malonic acid mono alkali salts

<u>Malonic acid mono Li salt</u>		<u>Malonic acid mono Na salt</u>		<u>Assignment</u>
<u>Parent</u>	<u>Deuterated</u>	<u>Parent</u>	<u>Deuterated</u>	
2965 m				} $\nu_{\text{CH}_2}$ } $\nu_{\text{OH}}$
2950 m	2935 m			
2910 m	2870 mb			
2700 w	2780 mb			
2550 m	2480 mbv			
	2220 w		2200 m	} $\nu_{\text{CD}_2}$
	2200 m		2160 m	
	2150 w		2140 m	
	2050 m			
	1900 b		1980 mvb	$\nu_{\text{OD}}$
1910 mb		1850 mb		$\nu_{\text{OH}}$
1740 s	1740 s	1695 vs	1680 vs	} $\nu_{\text{C=O}}$
1680 s	1680 s			
1585 vsb	1585 vsb	1585 vsb	1580 vsb	$\nu_{\text{COO}^- \text{ asym.}}$
1435 m	1425 m			$\delta_{\text{CH}_2}$ , ( $\nu_{\text{CO}} + \delta_{\text{OH}}$ )
1375 sb	1375 sb	1390 s	1395 s	$\nu_{\text{COO}^- \text{ sym.}}$
			1312 m	( $\nu_{\text{CO}} + \delta_{\text{OD}}$ )
1290 m	1290 vs			$\text{CH}_2 \text{ wag.}$
1275 m	1255 s	1255 sh	1265 sh	( $\nu_{\text{CO}} + \delta_{\text{OH}}$ )
1180 m		1170 m		$\text{CH}_2 \text{ twist}$



Table VI ... continued

	1100 s		1102 s	} $\int$ CD <sub>2</sub> , ( $\int$ ) CO + $\int$ OD CD <sub>2</sub> wag.
	1060 m		1061 m	
	1047 w		1041 m	
1010 m	1010 m			$\int$ C-C CH <sub>2</sub> rock.
		970 m		
		950 m		
920 s	920 w	922 s		$\int$ OH(o.o.p.)
900 m	900 m			$\int$ C-C
	890 w	890 w	910 m	} CD <sub>2</sub> twist.
	870 w		882 w	
			862 w	
820 m	800 m	810 m	838 m	$\int$ COO <sup>-</sup>
			763 m	CD <sub>2</sub> rock.
755 m				CH <sub>2</sub> rock.
	740 sh		682 m	} $\int$ OD (o.o.p.)
	720 m			
	670 m			CD <sub>2</sub> rock.
640 m		663 m		$\int$ COOH.

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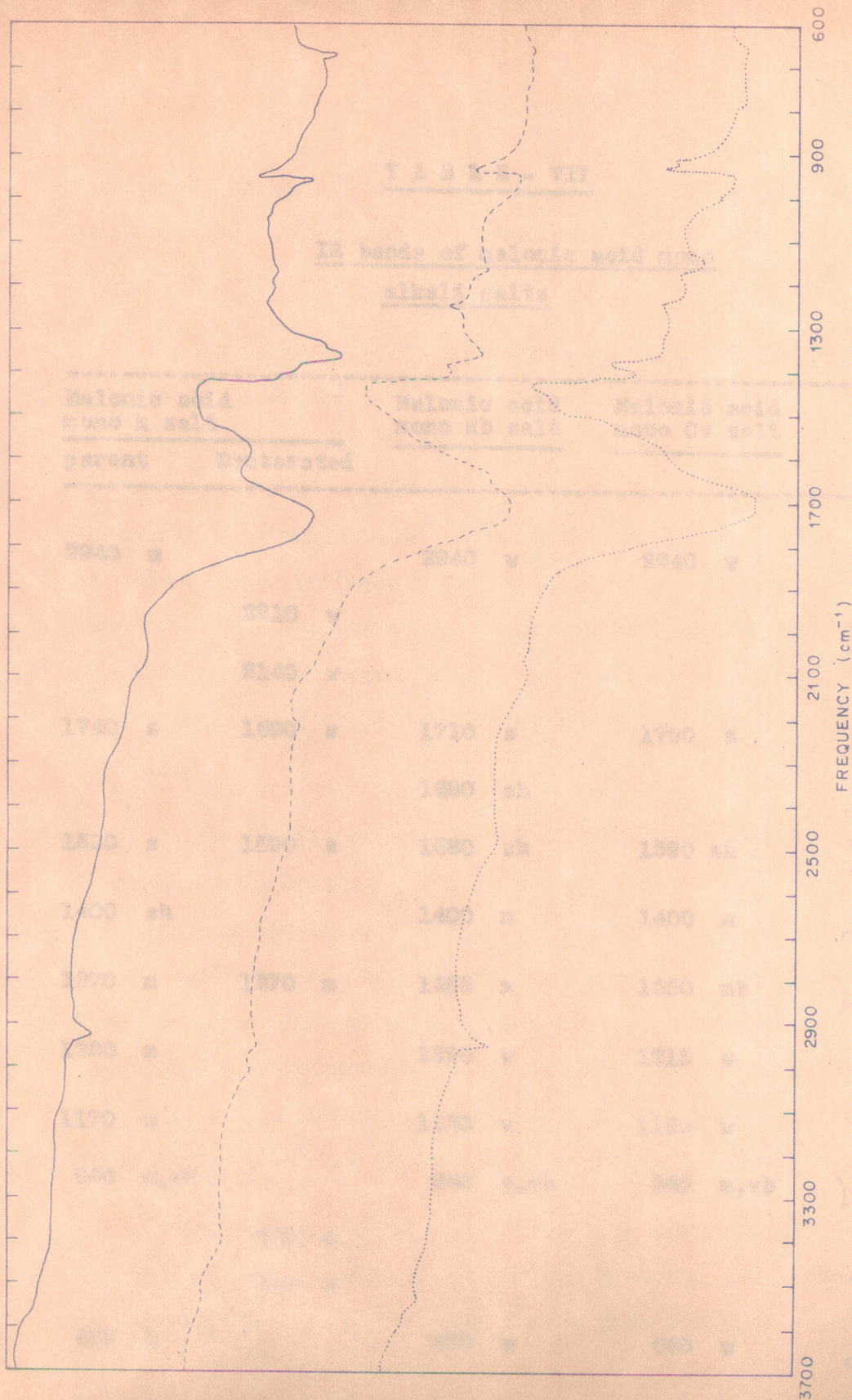


FIG. 9. IR SPECTRA OF MALONIC ACID MONO K SALT (—), MONO Rb SALT (---), MONO Cs SALT (.....)

← TRANSMITTANCE



T A B L E - V I I

IR bands of malonic acid mono  
alkali salts

<u>Malonic acid</u> <u>mono k salt</u>		<u>Malonic acid</u> <u>mono Rb salt</u>	<u>Malonic acid</u> <u>mono Cs salt</u>	Assignment
parent	Deuterated			
2940 m		2940 w	2940 w	$\nu_{\text{CH}_2}$
	2210 w			$\nu_{\text{CD}_2}$
	2140 w			
1740 s	1690 s	1710 s	1700 s	$\nu_{\text{C=O}}$ ,
		1680 sh		$\delta_{\text{OH}}$
1590 s	1590 s	1580 sh	1590 sh	$\nu_{\text{COO}^-}$ asym.
1400 sh		1400 m	1400 m	$\delta_{\text{CH}_2}$
1370 m	1370 m	1355 m	1350 mb	$\nu_{\text{COO}^-}$ sym.
1220 m		1220 w	1215 w	$\text{CH}_2$ wag.
1170 w		1160 w	1150 w	$\text{CH}_2$ twist.
960 m,vb		960 m,vb	960 m,vb	$\nu_{\text{OH}}$
	900 m			$\text{CD}_2$ wag.
	840 w			$\nu_{\text{OD}}$
670 m		670 w	660 w	$\delta_{\text{COOH}}$

symmetric hydrogen bond (Hadzi II). X-ray and neutron diffraction studies have established the presence of such a hydrogen bond in potassium hydrogen malonate<sup>14,15</sup>.

To understand the structure in solution the infrared spectra of these salts were recorded in DMSO solution. The spectrum of monopotassium salt of malonic acid in DMSO showed absorptions in the region 2800 - 1700  $\text{cm}^{-1}$  characteristic of a double minimum potential type comparable to the spectrum of mono sodium salt of malonic acid in DMSO. The PMR study showed the concentration dependence for the hydroxyl proton chemical shift (KH malonate 660-520 cps with respect to TMS at 60 M cps) in the range of 1-0.3% indicating the intermolecular nature of the hydrogen bonding.

Thus while an unsymmetrical intermolecular hydrogen bonding exists in the Li and Na salts a symmetrical intermolecular hydrogen bonding occurs in the K, Rb and Cs salts of malonic acid in the solid state. The higher ionic radii of the latter alkali ions favour a symmetrical hydrogen bonding. However, in DMSO solution the hydrogen bonding is intermolecular and unsymmetrical in nature in all the alkali salts. The concentration dependence shows that carboxylic OH is hydrogen bonded to DMSO.

Some support to the different hydrogen bonding in Li and Na hydrogen malonates was derived from the preliminary X-ray crystallographic investigation<sup>32</sup> of sodium hydrogen malonate.

As expected its crystal structure differed from the monoclinic potassium salt<sup>14</sup> with space group  $C_{2/m}$ . Sodium hydrogen malonate crystallized in orthorhombic form with space group  $Pbca$ ,  $z = 8$  and with cell dimensions of  $a = 6.79 \pm 0.03\text{\AA}$ ,  $b = 10.30 \pm 0.02\text{\AA}$  and  $c = 16.18 \pm 0.06\text{\AA}$   $\alpha = \beta = \gamma = 90^\circ$ .

In the monoalkali salts of oxydiacetic acid, a similar change in the nature of hydrogen bonding has been found between the potassium salt and rubidium salt, Li and Na salts being isomorphous with the former and the Cs and Tl salts isomorphous with the latter. A combined X-ray and neutron diffraction analysis<sup>17,18</sup> revealed that an intermolecular unsymmetrical hydrogen bond ( $2.476\text{\AA}$ ) was present in the potassium salt and an intermolecular symmetrical hydrogen bond ( $2.449\text{\AA}$ ) existed in the Rb salt. The larger ionic radii of the latter are responsible for the change in the packing of the infinite hydrogen oxydiacetate chains enhancing the symmetry of the structure. In the monoalkali salts of malonic acid as shown above the change from the unsymmetrical to symmetrical hydrogen bond is taking place at a lower ionic radius namely between  $\text{Na}^+$ ,  $0.95\text{\AA}$  and  $\text{K}^+$ ,  $1.33\text{\AA}$ . Only a detailed crystallographic investigation can throw more light on the nature of the change.

It is thus evident that in the monoalkali salts of these dicarboxylic acids, with increasing ionic radius of the cation, there is a tendency towards higher symmetry resulting in symmetric hydrogen bonding.

## C O N C L U S I O N S

The present study has clearly established that the unusually high values for ratio of dissociation constants (in water) in certain malonic and succinic acids is attributable to the formation of strong intramolecular hydrogen bonding between the carboxylic OH and the carboxylate COO<sup>-</sup> groups. Thus while strong symmetrical intramolecular hydrogen bonding is found in the diethyl and di-n-propyl malonic acid (121000, 277000) mono potassium salts, a weaker unsymmetrical hydrogen bond is found in the monoalkyl (ethyl and n-pentyl) and dimethyl (783) derivatives in the solid state. In a solvent similar to water e.g. dimethyl sulphoxide the strong intramolecular hydrogen bonding was unaffected. The study of the solid samples and use of DMSO as solvent has considerable advantages over the infrared analysis in solvents like D<sub>2</sub>O, methanol, etc.

A Courtalds model study confirmed how intermolecular contacts are made difficult due to the bulky substituents like ethyl, n-propyl in disubstituted malonic acids. Similar results were also obtained in the case of tetraalkyl succinic acids mono sodium salts where strong symmetrical intramolecular hydrogen bond was found in high  $k_1/k_2$  tetramethyl and tetra-n-propyl acids.

The role of ionic radius in intermolecular hydrogen bonding has been clearly brought out from the study of a series of monoalkali salts of malonic acid. While an intermolecular unsymmetrical hydrogen bond was found in salts with  $\text{Li}^+$  and  $\text{Na}^+$  ions, a symmetrical intermolecular hydrogen bond was found in salts with ions of higher ionic radii like  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ . This study thus confirms similar results with oxydiacetic acid stresses the importance of ionic radius of metal ion in deciding the nature of hydrogen bonding and hence packing in the crystal.

In conclusion the present work has shown how infrared and proton magnetic resonance spectral analyses are eminently suitable to characterise the two types of strong hydrogen bonds (Hadzi I and II). Their presence even in simple acid salts shows how common, after all, such strong hydrogen bonded compounds are!

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REFERENCES

1. D. H. McDaniel and H. C. Brown,  
Science (1953), 118, 370.
2. E. A. Braude and F. C. Nachod,  
"Determination of Organic Structures by Physical  
Methods"- Academic Press Inc. New York (1955).
3. L. Ebersson, Acta Chem, Scand, (1959) 13, 224.
4. L. Ebersson and S. Forsen,  
J. Phys. Chem., (1960) 64, 767.
5. S. N. Das and D. J. G. Ives,  
Proc. Chem, Soc. (1961) 373.
6. D. R. Lloyd and R. H. Prince,  
Proc. Chem. Soc. (1961) 464.
7. B. Akermark, Acta Chem. Scand. (1961) 15, 985.
8. D. Chapman, D. R. Lloyd and R. H. Prince,  
J. Chem. Soc. (1964) 550.
9. P. K. Glasoe and J.R. Hutchison,  
J. Phys. Chem. (1964) 68, 1562.
10. E. S. Hanrahan, Spectrochim Acta, (1966) 22, 1243.
11. M. H. Miles, E. M. Eyring, W. W. Eostein and  
R. E. Ostlund, J. Phys. Chem. (1965) 69, 467.
12. H. B. Evans and J. H. Goldstein,  
Spectrochim Acta A (1968) 24, 73.
13. D. Hadzi and A. Novake,  
Nuovo Cimento (1955) 11, Suppl. No.3, 715  
(C.A., 55, 172151).
14. J. O. Sime, J.C. Speakman and R. Parthasarathy,  
J. Chem.Soc. A. (1970) 1919.
15. M. Currie and J.C. Speakman,  
J. Chem. Soc. A (1970) 1923.
16. A. A. Belhekar and C. I. Jose,  
Ind. J. Chem. (1974) 12, 997.
17. J. Albertson, I. Grenthe and H. Herbertsson,  
Acta Cryst. B (1973) 29, 1855, 2839.
18. J. Albertsson, I. Grenthe and H. Herbertsson,  
Acta Cryst. B (1973) 29, 2751.

19. G. Hersberg, Infrared and Raman Spectra of Polyatomic Molecules"- D. Van Nostrand, 1945.
20. D. Hadzi and N. Sheppard,  
Proc. Roy, Soc. A (1954) 216, 247.
21. G. C. Pimentel and A. L. McClellan  
"The Hydrogen Bond"  
W. H. Freeman and Co. San Francisco, 1960.
22. D. Hadzi, Hydrogen Bonding , Pergamon Press, London,
23. M. D. Joesten and L. J. Sehaad,  
"Hydrogen Bonding"  
Marcel Dekker Inc. New York, 1974.
24. S. N. Vinogradov and R. H. Linnell,  
"Hydrogen Bonding"  
Van Nostrand Reinhold, 1971.
25. D. Hadzi, Pure and Appl. Chem. (1965), 11, 435.
26. B. D. Sharma and A. B. Biswas,  
Anal. Chem. (1958) 30, 1356.
27. M. Conrad, Ann. dev Chem. (1880) A204. 134.
28. C.S. Sehoepfle, J. Am. Chem. Soc. (1925) 47., 1473.
29. D. Hadzi. B. Orel and A. Novak,  
Speetrochim Acta A (1973) 29, 1745.
30. S. Forsen, J. Chem. Phys. (1959) 31, 852.
31. S.F. Darlow and W. Cochran,  
Acta Cryst, (1961)14 , 1250.
32. S. Y. Natu and M. C. Takwale,  
Unpublished results.