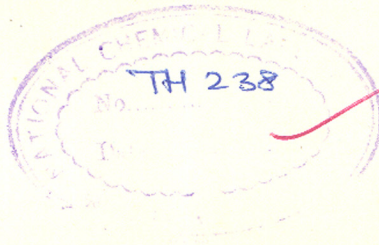
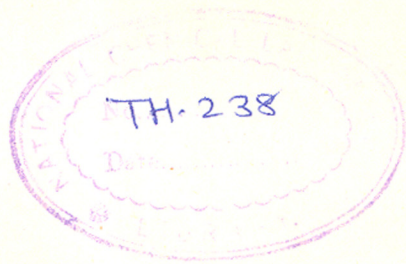


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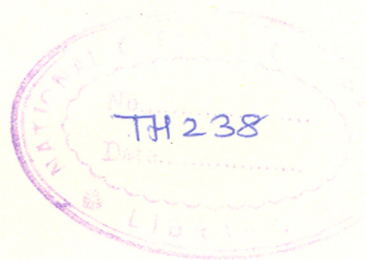
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INVESTIGATIONS ON  
THE VIBRATIONAL FREQUENCIES OF  
 $-\text{N}(\text{CH}_3)_2$  AND  $-\text{N}^+(\text{CH}_3)_3$  GROUPS

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



543.422.4 : 547.551(043)  
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COMPUTERISED

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

I wish to express my deep sense of gratitude to Dr. C. I. Jose for his guidance and encouragement during the course of this investigation.

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*Mangala S. Agashe*  
(Mangala S. Agashe)

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## CHAPTER - I

### INTRODUCTION

Skeletal vibrational frequencies of tertbutyl and isopropyl groups are well established and used extensively<sup>1</sup> for identifying these groups in hydrocarbons. It was Simpson and Sutherland<sup>2,3</sup> who made a detailed investigation of skeletal frequencies of these groups using valence force field. Their calculations showed that  $(\text{CH}_3)_3\text{C-Z}$  would give rise to a band at  $1250\text{ cm}^{-1}$  from a perpendicular asymmetric skeletal stretching mode  $\nu_2$  and another at  $1200\text{ cm}^{-1}$  due to parallel skeletal mode  $\nu_3$  which depended on the mass of 'z'. In neopentane, the increased symmetry would result in the coalescing of the two bands into a single band at  $1250\text{ cm}^{-1}$ . In the large number of paraffins examined, these predictions were found to be correct. The strong absorption bands near  $900\text{ cm}^{-1}$  found in compounds containing tertbutyl group were then assigned to  $\text{CH}_3$  rocking modes. Rasmussen<sup>4</sup> following earlier work however assigned the bands at  $1250\text{-}1200\text{ cm}^{-1}$  to  $\text{CH}_3$  rocking modes and those at  $900\text{ cm}^{-1}$  to skeletal stretching modes.

Similarly for isopropyl group  $(\text{CH}_3)_2\text{-CH-Z}$  their calculations<sup>2,3</sup> predicted two skeletal vibrational modes at  $1170$  and  $1140\text{ cm}^{-1}$ , the former of which was independent of the mass

of Z while the latter depended on it. These results were also found to be in agreement with observed spectra of many compounds containing this group. Later studies<sup>5</sup> on isobutane-d<sub>10</sub> and neopentane-d<sub>12</sub> along with a detailed normal coordinate analysis have proved these assignments to be correct.

The earliest study on compounds containing  $-\text{N}(\text{CH}_3)_3^+$  and  $-\text{N}(\text{CH}_3)_2$  groups which are similar to the above was by Edsall<sup>6</sup> in 1937. He assigned bands at  $1000-930 \text{ cm}^{-1}$  in trimethyl ammonium chloride and tetramethyl ammonium chloride ~~and tetramethyl ammonium chloride~~ to asymmetric C-N stretching mode. In dimethylamine and dimethylammonium chloride a band at  $1100-1000 \text{ cm}^{-1}$  was similarly assigned to the asymmetric CN stretching mode based on the polarisation behaviour of certain Raman spectral bands and the earlier assignments of the corresponding hydrocarbons by Kohlrausch ~~et al.~~<sup>7,8</sup>. However, he obtained low values of force constant for C-C bond in neopentane and C-N bond in tetramethyl ammonium chloride from these skeletal frequencies near  $1000 \text{ cm}^{-1}$ . Barcello and Bellanato<sup>9</sup> had also concluded that C-N symmetrical valence mode lay in the range  $1050-850 \text{ cm}^{-1}$  and asymmetrical mode at  $1050-1000 \text{ cm}^{-1}$  in mono, di and trimethyl amines. The bands above  $1100 \text{ cm}^{-1}$  were assigned by them to CH<sub>3</sub> rocking mode as intensity of these bands increased with addition of methyl groups.

Ebsworth and Sheppard<sup>10</sup> have studied the IR spectra of mono, di, tri and tetramethyl ammonium chlorides. By comparison with the spectra of corresponding hydrocarbons, the bands near  $1250\text{ cm}^{-1}$  were assigned to methyl rocking and those near  $950\text{ cm}^{-1}$  to C-N stretching in trimethyl ammonium iodide. However, in tetramethyl ammonium iodide, the assignments were reversed and bands near  $1280$  and  $950\text{ cm}^{-1}$  were assigned to asymmetric skeletal stretching mode and  $\text{CH}_3$  rocking mode respectively. Lorenzelli and Möller<sup>11</sup>, Bottger- and Geddes<sup>12</sup>, and Krishnamurthy<sup>13</sup> have assigned bands near  $1250$  and  $950\text{ cm}^{-1}$  in tetramethyl ammonium halides to  $\text{CH}_3$  rocking and C-N stretching modes respectively.

In glycine betaine and some of its derivatives, bands near  $950$  and  $1300-1100\text{ cm}^{-1}$  were ascribed<sup>14</sup> to  $\text{C}_3\text{N}$  asymmetrical stretching and methyl rocking modes respectively. Van Senden<sup>15</sup> has studied the IR spectra of series of n-alkyl trimethyl ammonium halides  $\text{R-N}(\text{CH}_3)_3\cdot\text{Hal}$  where  $\text{R} = \text{CH}_3, \text{C}_7\text{H}_{15}$  etc. and their  $\text{N}^{15}$  analogues. From the high intensity of the bands near  $950\text{ cm}^{-1}$  ascribable to the vibration of a polar bond and shift to lower frequency on change to  $\text{N}^{15}$ , these were assigned to  $\text{C}_3\text{N}$  stretching mode. Hume et al.<sup>16</sup> have studied the IR spectra of various n-alkyl or aryl trimethyl ammonium iodides. From the constancy of the position of the band near  $950\text{ cm}^{-1}$ , it was assigned to characteristic  $\text{C}_3\text{N}$  stretching vibration of  $\text{N}^+(\text{CH}_3)_3$  group.



Anhouse and Tobin<sup>17</sup> who studied the Raman spectra of tetramethyl ammonium iodide and hydroxide came to similar conclusions. Harmon<sup>18</sup> et al. have studied the effect of the crystal symmetry on the absorption frequencies of the tetramethyl ammonium ion in compounds with different anions. Assuming the earlier assignments of bands near  $950\text{ cm}^{-1}$  for C-N asymmetrical stretching mode, they found that the multiple structure of this band could be explained on its site symmetry. In the spectral assignments of trimethyl amine oxide<sup>19</sup> supported by normal coordinate treatment, the band at  $955\text{ cm}^{-1}$  was assigned to  $C_3N$  asymmetric stretching mode.

Regarding the assignments of vibrational modes of  $N(CH_3)_2$  group, Edsall's<sup>6</sup> work has already been discussed. Subsequently, in dimethyl amine, Gamer and Wolff<sup>20</sup> assigned bands at 1022, 900 and  $1100-1250\text{ cm}^{-1}$  to asymmetric and symmetric  $C_2N$  stretching and methyl rocking modes respectively. In dimethyl aniline the bands at 1343, 1057,  $943\text{ cm}^{-1}$  were assigned<sup>21</sup> to aromatic C-N stretching,  $C_2N$  antisymmetric stretching and  $C_2N$  symmetric stretching modes respectively. From a study of compounds containing dimethyl amino group, Katritzky and Jones<sup>22</sup> assigned the bands near 1050 and  $950\text{ cm}^{-1}$  to asymmetric and symmetric  $C_2N$  stretching modes and those at  $1100-1200\text{ cm}^{-1}$  to  $CH_3$  rocking modes. Later the effect of change in mass of X on the spectra of compounds containing dimethylamino group  $XN(CH_3)_2$  was studied<sup>23</sup>. The asymmetric

stretching mode of  $C_2N$  skeleton assigned to a band near  $1000\text{ cm}^{-1}$  was found to be independent of the mass<sup>of X</sup>. Of the bands near  $1220\text{ cm}^{-1}$  and  $1160-1050\text{ cm}^{-1}$  ascribed to methyl rocking, the latter was found to be extremely mass sensitive. The symmetric stretching mode of  $NC_2$  skeleton was assigned to the band near  $950\text{ cm}^{-1}$ . For dimethyl amino group attached to aromatic ring, relationship has been found<sup>24</sup> between the frequency of the band and angle between  $NCC$  plane and aromatic ring, which would be responsible for variable mixing of vibrational modes. They have assigned the bands at  $1350-1300\text{ cm}^{-1}$  to  $\delta$  C-N aromatic,  $1250-1100\text{ cm}^{-1}$ ,  $1180-1150\text{ cm}^{-1}$  and  $1130-1100\text{ cm}^{-1}$  to the three rocking modes, a band near  $1058\text{ cm}^{-1}$  to  $\nu$   $C_2N$  asymmetric and  $960-940\text{ cm}^{-1}$  to  $C_2N$  symmetric stretching modes respectively.

Recent studies on trimethyl sulphoxonium iodide<sup>25</sup>, trimethyl arsine oxide<sup>26</sup> and their  $CD_3$  analogues showed methyl rocking modes and skeletal modes to absorb at very different regions of the spectra than mentioned above. Thus bands at  $1222-945$  and  $938-837\text{ cm}^{-1}$  were ascribed to rocking modes in the former and latter modes respectively. Since a survey of the literature showed absence of any study of  $-N^+(CH_3)_3$  and  $-N(CH_3)_2$  groups along with their  $CD_3$  analogues, which only could decide these modes unequivocally, the spectra of a large number of compounds  $R-N^+(CH_3)_3I^-$  where R=alkyl or aryl group

and  $R-N(CH_3)_2$  where R was an aryl group, were therefore analysed along with their  $CD_3$  analogues and forms the subject matter of this thesis.

C H A P T E R - II

THEORY OF VIBRATIONAL SPECTRA

II a : VIBRATIONAL ENERGY

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

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

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

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

$$E_v = (v + 1/2)h\nu_e - (v + 1/2)^2 h\nu_e \chi_e$$

where  $v$  = vibrational quantum number, 0, 1, 2, etc.  $\nu_e$  = vibrational frequency,  $\chi_e$  = anharmonicity constant.

Since the difference in energy between the vibrational ground state and first excited state is high compared to  $kT$  at room temperature, according to Boltzmann's distribution law, the excited state is very sparingly populated (1 in 10,000). Under such conditions, transitions to the 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 group during the vibration. Homopolar diatomic molecules like  $H_2$ ,  $O_2$ ,  $N_2$ , etc. and certain vibrations in symmetrical molecules where no change in dipole moment takes place during the vibration do not therefore give infrared spectra. Though the transitions from the ground state to the first excited state is the most probable, overtones ( $\Delta v = 2, 3$ , etc.) and combination modes are also observed.

## II b : DIATOMIC MOLECULE

For a diatomic molecule, the single mode of vibration is due to the stretching of the bond which may be approximated to two particles having masses  $m_1$  and  $m_2$  held by an elastic spring executing a simple harmonic motion (Hooke's Law). If  $x_1$  and  $x_2$  are the displacements of the atoms from the equilibrium positions, then the restoring force is given by  $F = -k(x_1 - x_2)$  where  $k$  is the force constant i.e. force per

unit displacement. The vibrational frequency of such a system is given by:

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

where  $\mu$  is the reduced mass of the system

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

## II c : POLYATOMIC 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 since the rotational motion can be described by 2 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). The complex motions of atoms as simplified by the normal vibrations can be determined by classical theory of vibrations.

## II d : NORMAL COORDINATE TREATMENT<sup>27</sup>

In a system of N particles each particle exerts a force on every other particle so that the total force on each particle is zero. If one particle is displaced from its equilibrium position by a distance whose components in the direction of the three fixed coordinates are  $x_1, y_1, z_1$ , there will be a restoring force whose components  $F_{x_1}, F_{y_1}, F_{z_1}$  would be given by the equations:

$$\begin{aligned} F_{x_1} &= -k_{xx}^{11}x_1 - k_{xy}^{11}y_1 - k_{xz}^{11}z_1 \\ F_{y_1} &= -k_{yx}^{11}x_1 - k_{yy}^{11}y_1 - k_{yz}^{11}z_1 \\ F_{z_1} &= -k_{zx}^{11}x_1 - k_{zy}^{11}y_1 - k_{zz}^{11}z_1 \end{aligned}$$

If the other particles of the system are also moving then there will be 3N terms in each of these equations and there will be 3N such equations.

If the normal vibration as defined earlier really involves the motions of all the particles in phase and with same frequency, then each of the components of the restoring forces should be equal to the product of  $4\pi^2\nu^2$ , the mass of the particle ( $m_1, m_2, \dots$  etc.) and the displacement coordinates ( $x_1, y_1, z_1, x_2, y_2, \dots$  etc.)

$$\begin{aligned} 4\pi^2\nu^2 m_1 x_1 &= k_{xx}^{11}x_1 + k_{xy}^{11}y_1 + k_{xz}^{11}z_1 + k_{xx}^{12}x_2 + k_{xy}^{12}y_2 \dots k_{xz}^{1N}z_N \\ 4\pi^2\nu^2 m_1 y_1 &= k_{yx}^{11}x_1 + k_{yy}^{11}y_1 + k_{yz}^{11}z_1 + k_{yx}^{12}x_2 + k_{yy}^{12}y_2 \\ &\quad + k_{yz}^{12}z_2 \dots k_{yz}^{1N}z_N \end{aligned}$$





## II e : CHARACTERISTIC GROUP FREQUENCIES<sup>27</sup>

Fairly constant vibrational frequencies observed for a specific group in different molecules are termed characteristic group frequencies which are extensively used to establish the presence of such groups in unknown compounds. Generally, when light atoms like hydrogen, deuterium, etc. are attached to heavy atoms like C, N, O, their motions (stretching, deformations etc.) give rise to such characteristic group frequencies. This can be understood since during the vibration, the heavy atom moves very little compared to the lighter one and therefore the influence of the vibration of the remaining part of the molecule on this motion is minimal. Apart from the case of the end light atoms discussed above, characteristic frequencies may be exhibited by two multiply bonded atoms of similar mass, when they are singly bonded to adjacent atoms (e.g. triple and double bonds lying adjacent to single bonds). While certain groups in a molecule can vibrate more or less independently by virtue of their differing masses and higher bond strengths, strong vibrational coupling between groups takes place when their vibrational frequencies are close to one another and related by appropriate symmetry. Thus if two groups are adjacent to one another, the angle between these determines the extent of their coupling, being least when these are at  $90^\circ$  to one another. Well known cases of this type of coupling are those of  $\text{-C-O}^{\text{H}}$  and  $\text{C-N}^{\text{H}}$  where the C-O and C-N stretching

modes have been found to couple strongly with O-H and N-H deformation modes respectively. The extent of coupling can be investigated in these cases simply by replacement of the hydrogen with deuterium.

#### II f : RAMAN SPECTRA

Vibrational spectra can also be obtained as Raman shifts in the feeble scattered light (at  $90^\circ$ ) when the sample is irradiated with monochromatic ultraviolet or visible radiation. Since Raman activity is due to a change in the polarizability of the molecule, as against the change in dipole moment in infrared, many vibrations inactive in the infrared (stretching of homopolar molecules etc.) are studied easily by the Raman spectra. The experimental convenience of studying spectra in an easily accessible region (ultraviolet, visible), low frequency vibrations and aqueous systems etc. has made it a worthy complimentary to the infrared spectra for study of molecular motions.

#### II g : CLASSIFICATION OF VIBRATIONS FOR $N^+(CH_3)_3$ AND $N(CH_3)_2$ GROUPS<sup>9,10</sup>

The first set of compounds for the present study  $RN^+(CH_3)_3I^-$  can be considered as consisting of an ion  $RN^+(CH_3)_3$  having  $C_{3v}$  symmetry. The total number of vibrational modes is 36. Out of them, 12 are doubly degenerate asymmetric modes,  $8A_1$  and  $4A_2$  modes. Out of the 12 asymmetric degenerate modes,

3 are skeletal (stretching, deformation and rocking) modes and the remaining have their origin in methyl groups (3 each stretching, deformations and rocking modes). Out of the  $8A_1$  modes, 3 are skeletal (stretching, deformation and  $\nu_{R-N}$ ) modes. The remaining five consist of two methyl stretching two methyl deformation and one methyl rocking modes. The four methyl  $A_2$  infrared inactive modes are one stretching, one deformation and two torsional modes.

In compounds  $R-N(CH_3)_2$  having  $C_s$  symmetry there are 24 fundamental vibrations out of which 12 are internal vibrations of the  $CH_3$  group (stretching and deformation), 6 are external vibrations ( $CH_3$  rocking, torsion) and the remaining six belong to the skeletal modes.

CHAPTER - IIIEXPERIMENTALPREPARATIONSIII a : Methyl iodide-d<sub>3</sub>

Trimethyl sulphoxonium iodide  $[(\text{CH}_3)_3\text{SOI}]$  was prepared<sup>28</sup> by refluxing dimethyl sulphoxide with 2.25 times methyl iodide for four days (yield - 55%). It was washed with chloroform and dissolved in just enough  $\text{D}_2\text{O}$  (99.8%, Atomic Energy Commission, Trombay) with 0.1 g. sodium carbonate to get a clear solution at  $90^\circ\text{C}$ . It was kept for 1 hour at that temperature and cooled to  $-5^\circ\text{C}$ . After two hours, the crystallized product was filtered out. This deuteration procedure was repeated three more times to obtain 99% deuterated salt as checked by its infrared spectrum in the  $\text{CH}_3/\text{CD}_3$  stretching region. This salt was decomposed<sup>29</sup> by heating to  $220^\circ\text{C}$  in a flask having a fractionating column, an ice cooled water condenser and two traps, cooled by chloroform-liquid nitrogen and ice salt mixtures. A pressure of 10 mm was maintained inside using a vacuum pump. Methyl iodide collected in the traps was then distilled carefully to obtain 97% deuterated  $\text{CD}_3\text{I}$  (3%  $\text{CD}_2\text{HI}$ ) as determined by its mass spectrum.

T A B L E - I

## MELTING POINTS AND MICROANALYSES RESULTS

Sr. No.	Compound	Molecular formula	Melting point	% Carbon		% Hydrogen	
				Found	Calc.	Found	Calc.
1.	Trimethyl, phenyl ammonium iodide	$C_9H_{14}NI$	224°C				
2.	Trimethyl, <i>o</i> -hydroxy phenyl ammonium iodide	$C_9H_{14}ONI$	190°C	39.67	38.7	5.09	5.02
3.	Trimethyl, <i>m</i> -hydroxy phenyl ammonium iodide	$C_9H_{14}ONI$	183°C	37.93	38.7	5.22	5.02
4.	Trimethyl, <i>p</i> -hydroxy phenyl ammonium iodide	$C_9H_{14}ONI$	189°C	38.85	38.7	5.11	5.02
5.	Trimethyl, butyl ammonium iodide	$C_7H_{18}NI$	220°C	34.42	34.58	7.48	7.40
6.	Trimethyl, hexyl ammonium iodide	$C_9H_{22}NI$	166°C	39.34	39.85	8.11	8.12
7.	Tetramethyl ammonium iodide	$C_4H_{12}NI$	> 300°C	24.18	23.88	6.30	5.97
8.	NN-dimethyl aniline	$C_8H_{11}N$	Liquid				
9.	<i>o</i> -Hydroxy NN-dimethyl aniline	$C_8H_{11}ON$	44°C				
10.	<i>m</i> -Hydroxy NN-dimethyl aniline	$C_8H_{11}ON$	83°C				
11.	<i>p</i> -hydroxy NN-dimethyl aniline	$C_8H_{11}ON$	74°C	69.18	70.1	7.71	8.03

III b : Trimethyl-phenyl, *o*-hydroxyphenyl, *m*-hydroxy phenyl, *p*-hydroxy phenyl ammonium iodides and their CD<sub>3</sub> analogues

These compounds were prepared<sup>30</sup> by refluxing (temp. ~70°C) the corresponding amino derivatives namely aniline, *o*-hydroxy aniline, *m*-hydroxy aniline, *p*-hydroxy aniline respectively and equimolar sodium carbonate with 3.2 times methyl iodide in methyl alcohol for 12 hours. The mixture was then left overnight in deep freeze. The precipitated solid was filtered, crystallized from water and dried at 110°C. The microanalyses and melting points are given in Table I. The corresponding CD<sub>3</sub> analogues were prepared following the same procedure using CD<sub>3</sub>I in place of CH<sub>3</sub>I.

III c : Trimethyl- hexyl and butyl ammonium iodides and their CD<sub>3</sub> analogues

For the alkyl derivatives the same procedure as for aryl derivatives was used except that 1.5 moles of sodium hydroxide<sup>31</sup> were used in place of sodium carbonate. The solid trimethyl- hexyl and butyl ammonium iodides (30% yield) were washed with methanol and recrystallized from it. These were found to be very hygroscopic and the spectra were recorded, after thorough drying at 110°C for at least an hour. The microanalyses results and melting points are given in Table I. The corresponding CD<sub>3</sub> analogues were prepared using CD<sub>3</sub>I.

543.422.4; 547.551(α43)

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### III d : Tetramethyl ammonium iodide and its CD<sub>3</sub> analogue

0.55 cc. Ammonia solution (28%) and 1 cc. methyl iodide were refluxed in 5 cc. of methyl alcohol for about 12 hours to obtain the tetramethyl ammonium iodide<sup>32</sup> which was hygroscopic and therefore dried at 110°C. The microanalysis result and melting point are given in Table I. The corresponding CD<sub>3</sub> analogue was prepared similarly using CD<sub>3</sub>I.

### III e : NN-dimethyl aniline and o, m, p hydroxy NN-dimethyl anilines and their CD<sub>3</sub> analogues

The corresponding methiodides were decomposed<sup>30</sup> in a flask with a bent side tube by heating under reduced pressure. The dimethyl amino derivatives condensed in the bent portion were freed from recombined methiodides by dissolution in CCl<sub>4</sub> or diethyl ether. The white crystalline amino derivatives were found to be very light sensitive, turning brownish black within a few hours. The microanalyses and melting points are given in Table I.

### III f : Instrumental

All the spectral measurements were carried out on a Perkin-Elmer Model 221, double beam spectrophotometer equipped with sodium chloride prism-grating interchange. The samples were examined as nujol and hexachlorobutadiene mulls and the carbon tetrachloride solutions (0.1 and 10 mm path length) in some cases. The instrument was calibrated with water vapour and carbon dioxide bands and the calibration was checked with polystyrene film each time.

C H A P T E R - I V

INFRARED SPECTRA OF PHENYL, o, m, p HYDROXY  
PHENYL, HEXYL AND BUTYL, TRIMETHYL AMMONIUM  
IODIDES, TETRAMETHYL AMMONIUM IODIDE AND  
THEIR  $CD_3$  ANALOGUES

---

IV a : RESULTS AND DISCUSSION

The infrared spectra of phenyl, o, m, p hydroxy phenyl, hexyl and butyl, trimethyl ammonium iodides and tetramethyl ammonium iodide and their  $CD_3$  analogues are presented in Figs. 1 to 7 and the absorption bands and their assignments are tabulated in Tables II and III. The discussion is restricted to the assignments of the  $N(CH_3)_3^+/N^+(CD_3)_3$  groups; bands due to the remaining part of the molecule are too well known and therefore ascribed on the basis of reported literature data<sup>33</sup>. Except for the tetramethyl ammonium iodide, the spectra of the remaining compounds have not been reported in literature. Even in the former, the spectrum of the  $CD_3$  analogue has not been studied. The spectrum of the tetramethyl ammonium iodide is in agreement with the reported spectrum<sup>10</sup>.

IV b : METHYL STRETCHING BANDS

All the above compounds showed three to four weak bands along with a medium strong band in the region 3050-2750  $cm^{-1}$  against the expected five bands. While the intensity



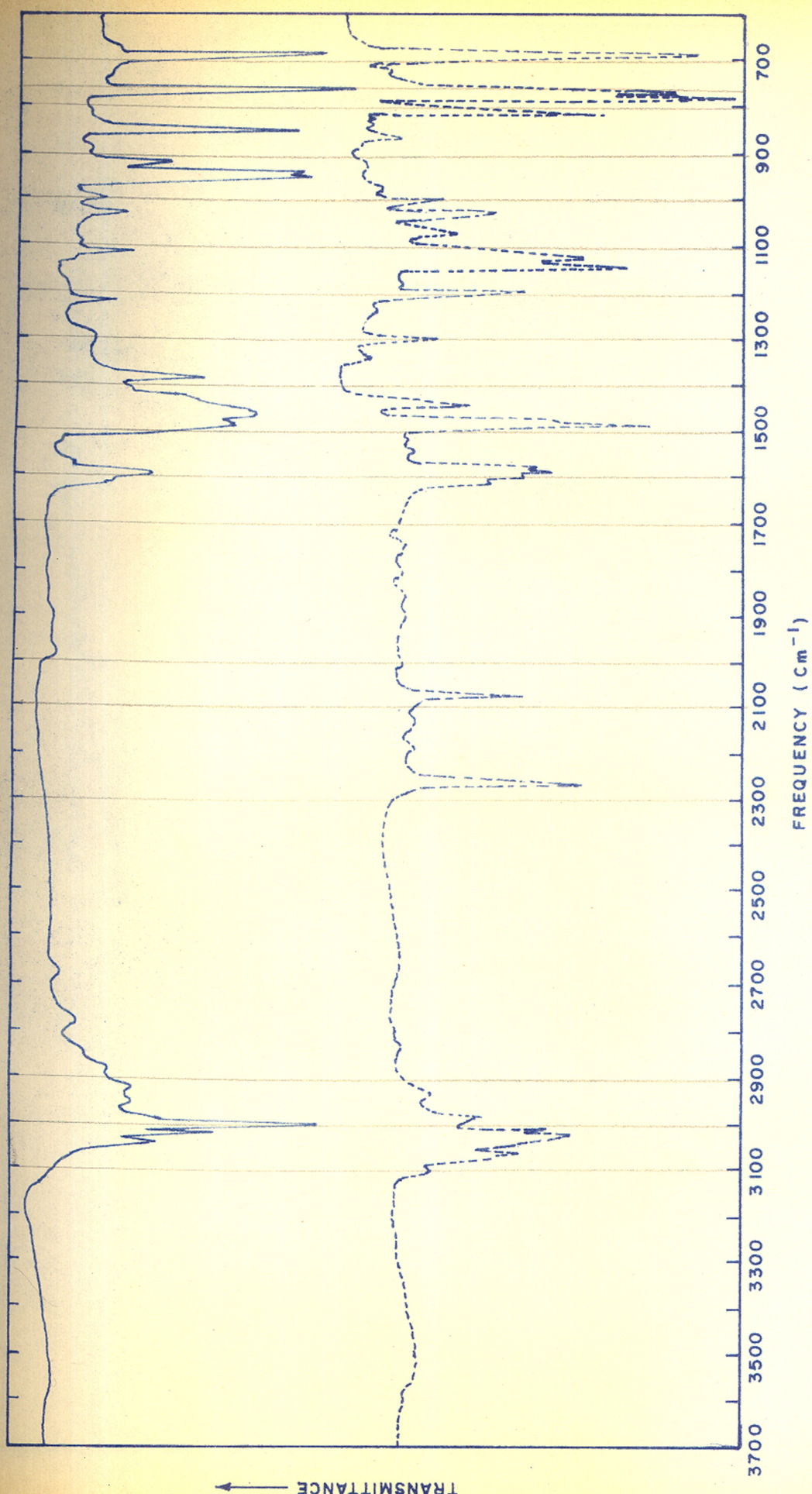


FIG. 1. IR SPECTRA OF TRIMETHYL PHENYL AMMONIUM IODIDE ( — )  
 CD<sub>3</sub> ANALOGUE ( - - - )

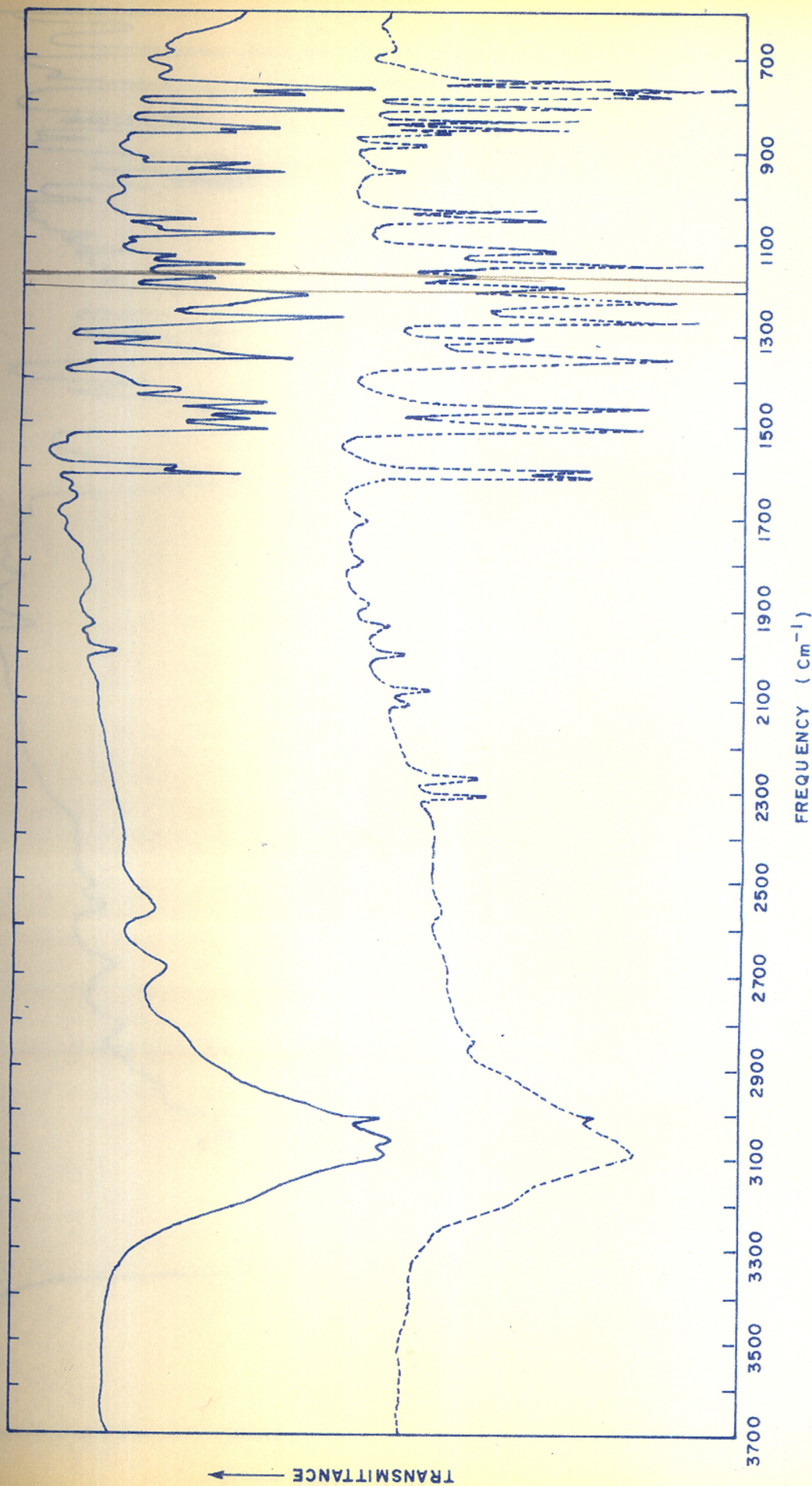


FIG. 2. IR SPECTRA OF TRIMETHYL O-HYDROXY PHENYL AMMONIUM IODIDE (—)

$\text{CD}_3$  ANALOGUE (-----)

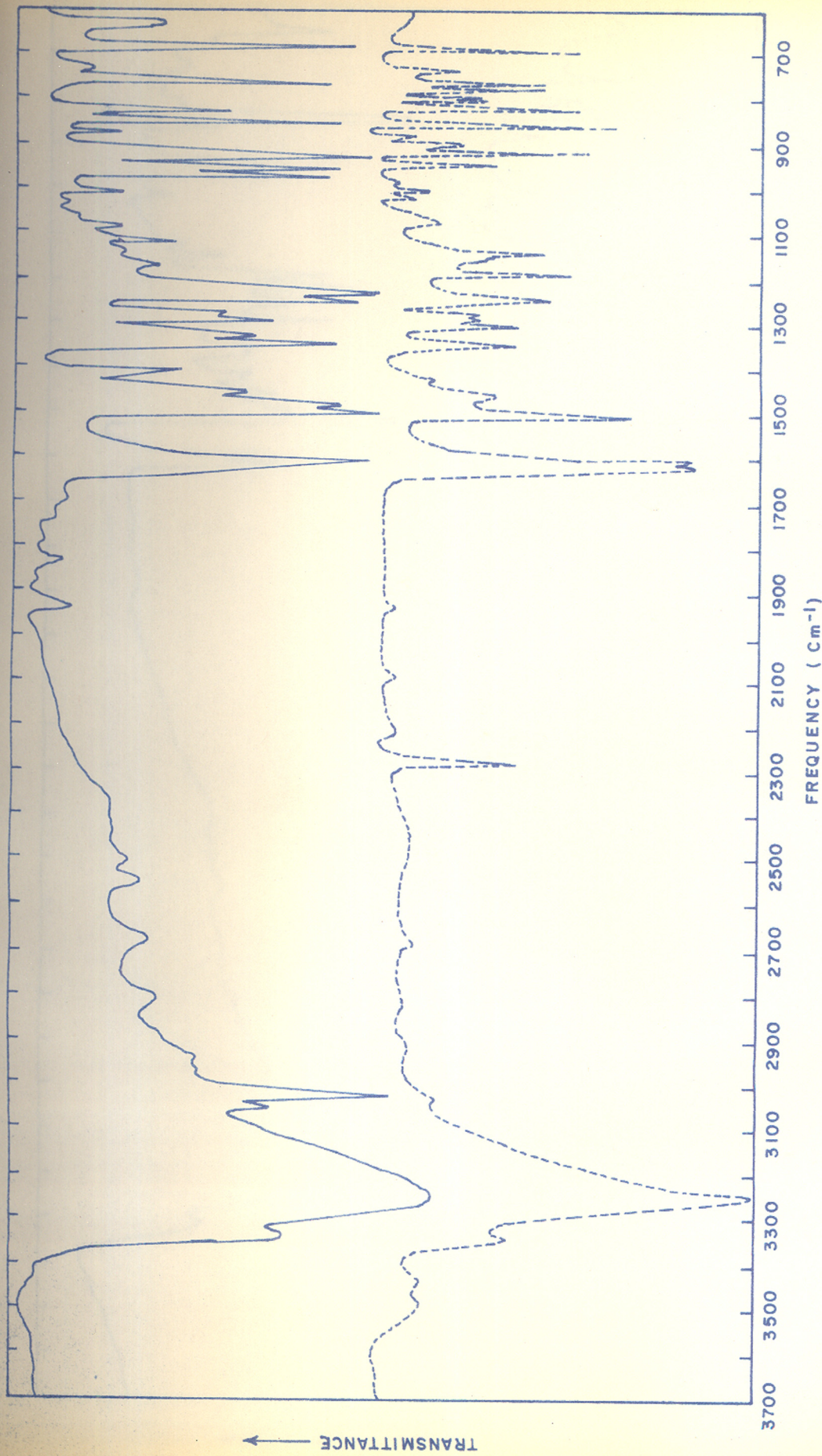


FIG. 3. IR SPECTRA OF TRIMETHYL M-HYDROXY PHENYL AMMONIUM IODIDE (——) CD<sub>3</sub> ANALOGUE ( - - - - )

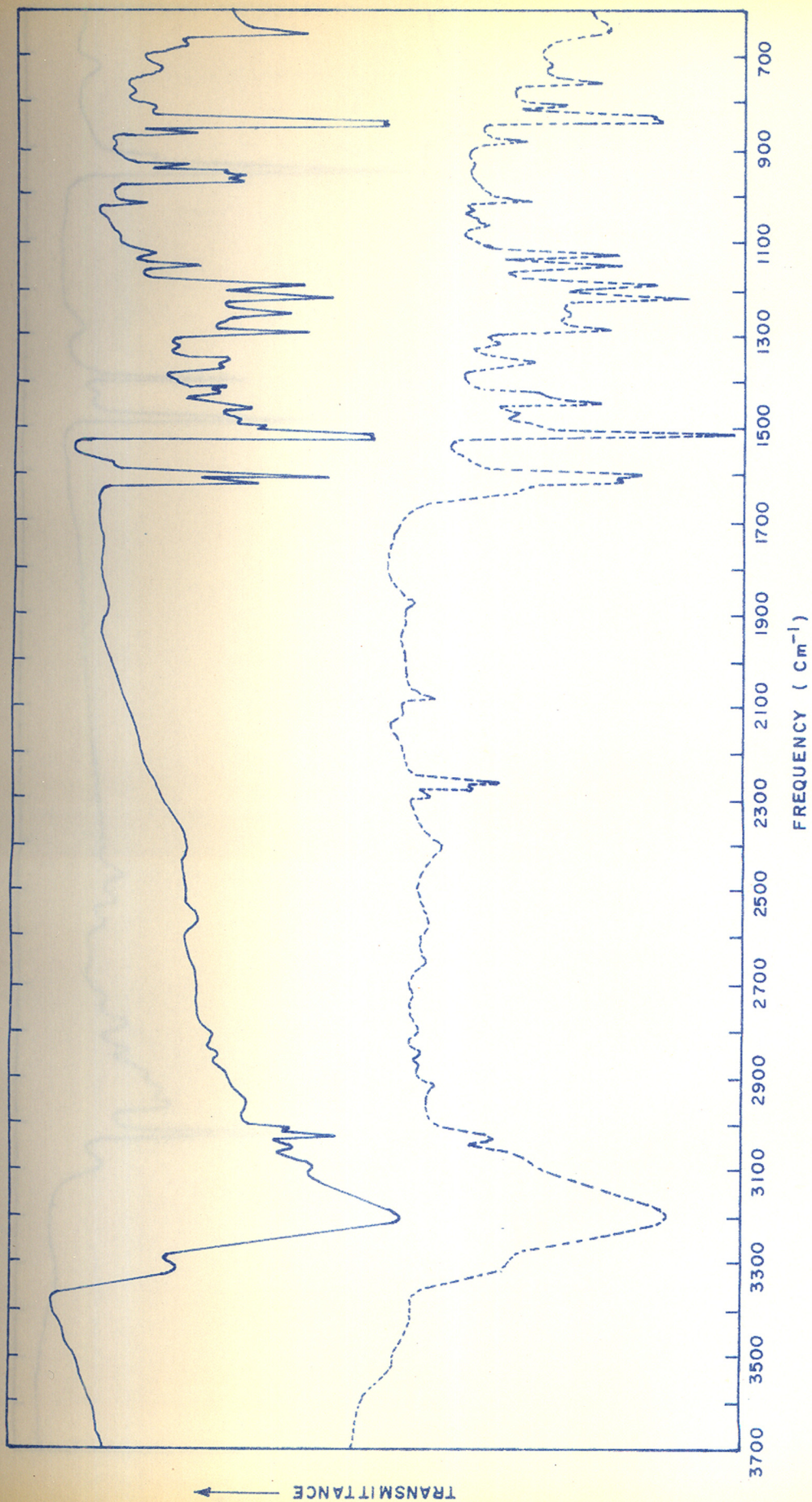


FIG. 4. IR SPECTRA OF TRIMETHYL p-HYDROXY PHENYL AMMONIUM IODIDE

( ——— )

CD<sub>3</sub> ANALOGUE

( - - - - )

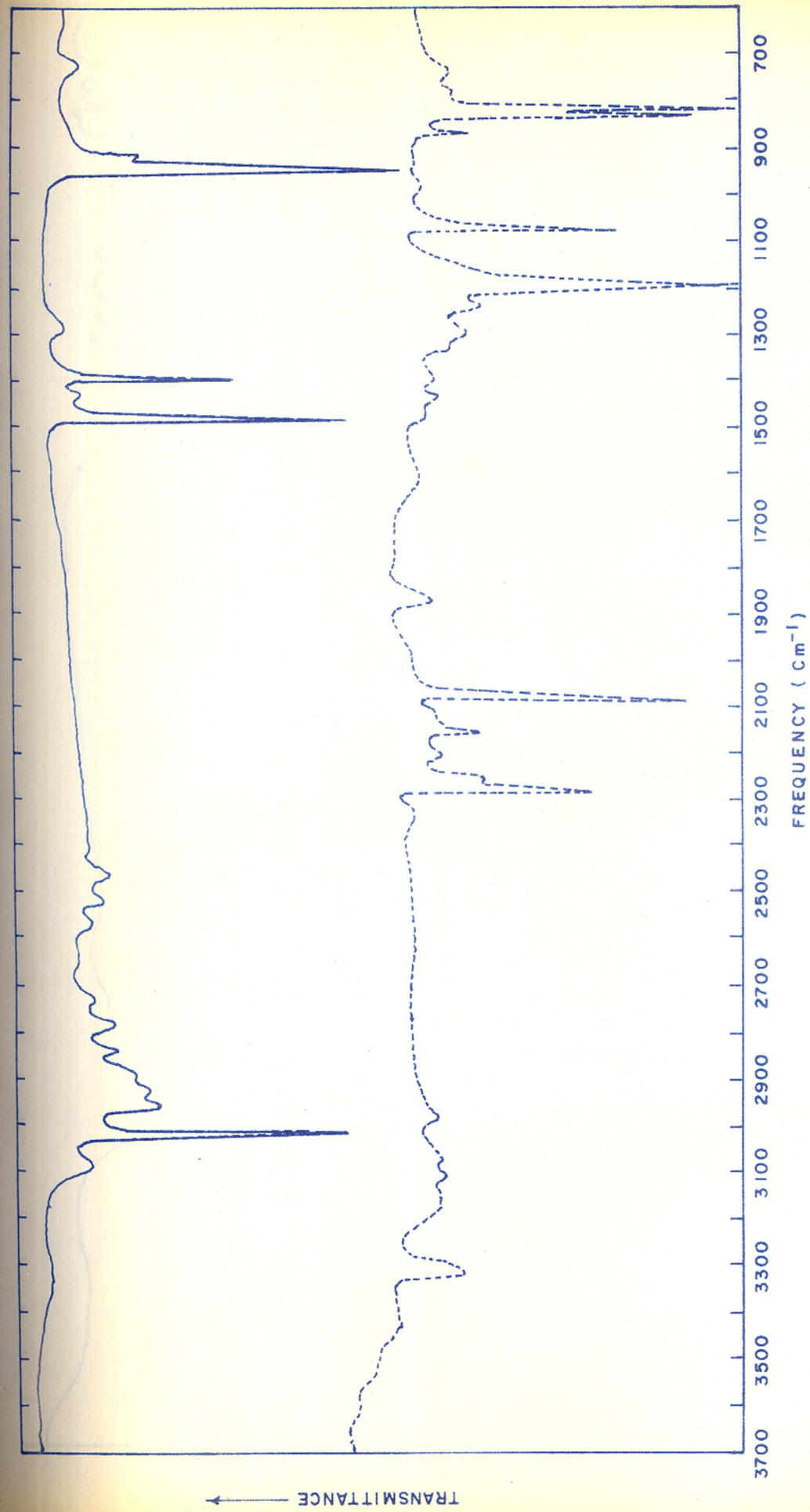


FIG. 5. IR SPECTRA OF TETRAMETHYL AMMONIUM IODIDE ( — )  
CD<sub>3</sub> ANALOGUE ( - - - )

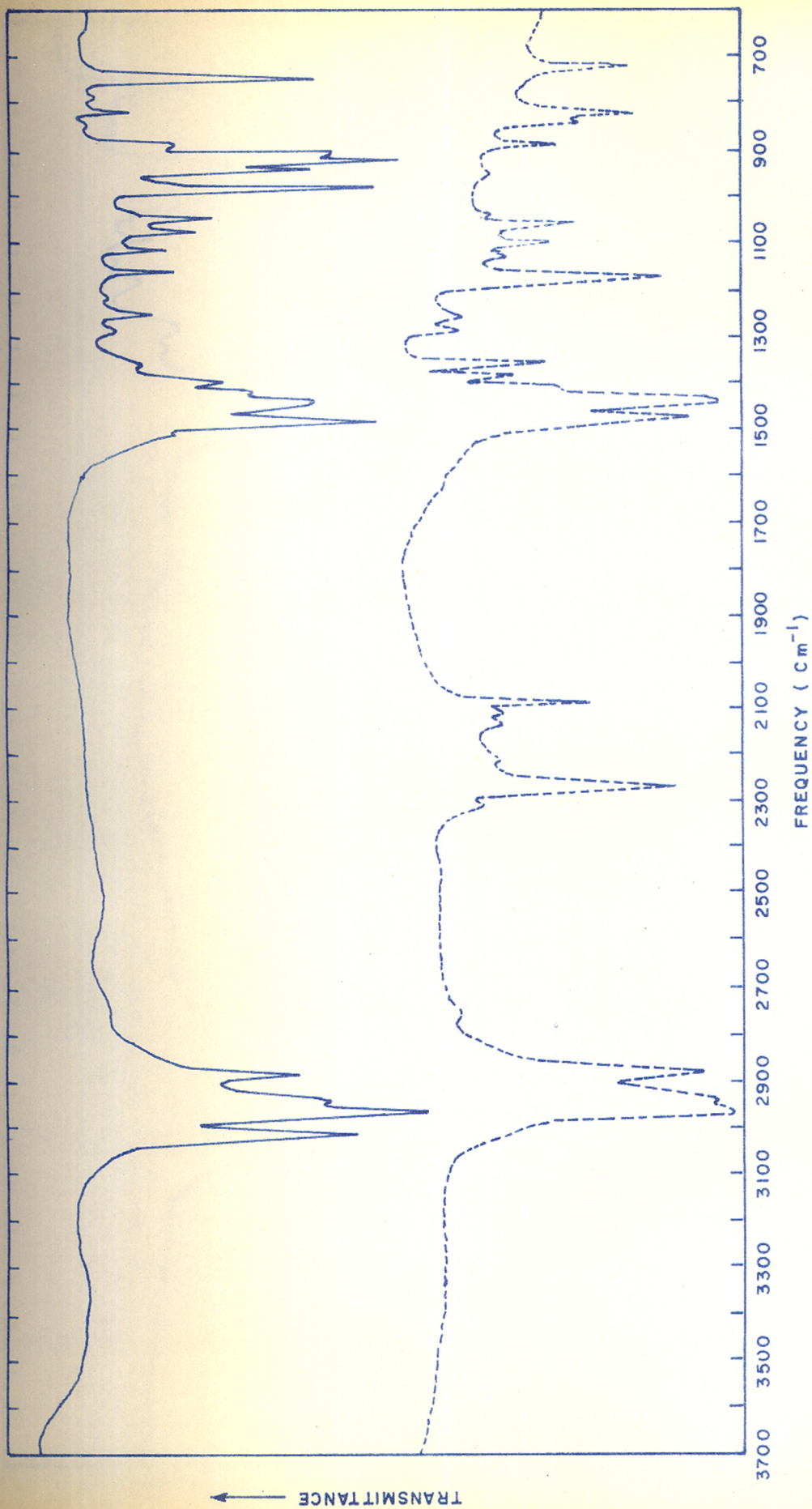


FIG. 6. IR SPECTRA OF TRIMETHYL BUTYL AMMONIUM IODIDE ( — )  
 $\text{CD}_3$  ANALOGUE ( - - - )

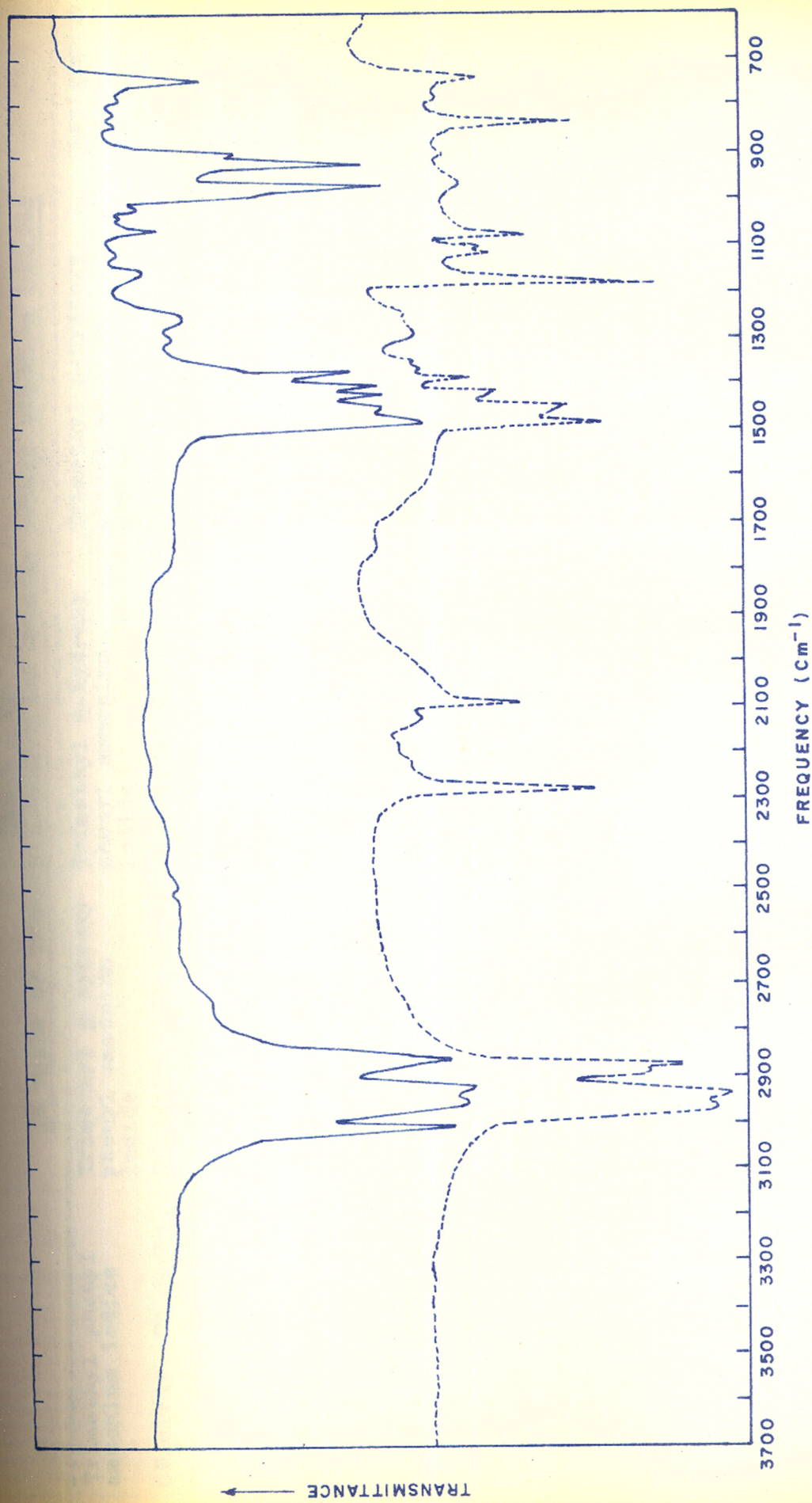


FIG. 7. IR SPECTRA OF TRIMETHYL HEXYL AMMONIUM IODIDE (—)  $\text{CD}_3$  ANALOGUE (---)

TABLE - II

## IR BANDS OF TRIMETHYL-PHENYL AND HYDROXY PHENYL AMMONIUM IODIDES

Trimethyl phenyl ammonium iodide		Trimethyl <i>o</i> -hydroxy phenyl ammonium iodide		Trimethyl <i>m</i> -hydroxy phenyl ammonium iodide		Trimethyl <i>p</i> -hydroxy phenyl ammonium iodide		Assignments
CH <sub>3</sub> deriv. CD <sub>3</sub> deriv.		CH <sub>3</sub> deriv. CD <sub>3</sub> deriv.		CH <sub>3</sub> deriv. CD <sub>3</sub> deriv.		CH <sub>3</sub> deriv. CD <sub>3</sub> deriv.		
3055 m	3055 m	3185 sh	3180 sh	3240 m	3240 s	3300 m	3300 m	} OH
3030 m	3030 m	3080 s	3090 s	3240 s	3235 s	3180 s	3190 s	
3010 s	3010 m	3060 s	3050 sh	3035 m	3030 vw	3065 s	3065 sh	} CH aromatic
2950 w	3010 m	3010 s	3030 sh	3015 s	3010 s	3030 s	3030 m	
2930 w	3010 m	2950 sh	3030 sh	2950 w	3000 m	3010 s	3000 m	} CH <sub>3</sub> [N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> ]
2870 w	3010 m	2850 w	3030 sh	2850 w	2960 w	3010 s	2960 w	
2785 w	3010 m	2810 w	3030 sh	2805 w	2810 w	2810 w	2810 w	} Σ (C-O-H)
	3010 m	2680 w	3030 sh	2680 w	2680 vw	2680 w	2650 vw	
	3010 m	2555 w	3030 sh	2550 vw	2550 vw	2550 w	2550 vw	} CD <sub>3</sub> [N <sup>+</sup> (CD <sub>3</sub> ) <sub>3</sub> ]
	3010 m	2680 w	3030 sh	2680 w	2680 vw	2680 w	2650 vw	
	3010 m	2305 m	3030 sh	2305 m	2305 m	2305 m	2290 w	} CD <sub>3</sub> [N <sup>+</sup> (CD <sub>3</sub> ) <sub>3</sub> ]
	3010 m	2270 m	3030 sh	2270 m	2270 m	2270 m	2260 m	
	3010 m	2105 w	3030 sh	2105 w	2250 sh	2250 sh	2250 sh	
	3010 m	2080 m	3030 sh	2080 m	2070 w	2070 w	2080 w	



Table II .. continued

1625 m	1620 m	1602 s	1605 s	1610 s	1620 s	1610 m	1610 s		
1605 s	1590 m	1592 s	1592 s	1600 sh	1610 s	1595 s	1595 s	C-C aromatic	
1498 m	1490 m	1510 s	1505 s	1480 s		1510 s	1510 s		
1480 m	1480 sh		1465 w	1465 m	1465 m	1475 m	1475 m		
1465 m		1485 m	1480 s	1490 s		1450 m	1450 m	$\delta$ CH <sub>3</sub> asym. [N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> ]	
		1470 m							
1450 m	1455 m	1450 m	1455 m	1448 m	1448 m	1440 sh	1440 m	C-C aromatic	
1400 m		1420 m		1408 m		1405 m	1405 m	$\delta$ CH <sub>3</sub> sym. [N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub> ]	
		1350 s	1350 s	1330 m	1330 m	1355 m	1345 m	(C-O + $\delta$ O-H)	
		1330 sh	1330 sh						
1300 w	1300 m	1310 m	1310 m	1315 m	1315 sh	1310 w	1315 w	C-N aromatic.	
		1280 sh	1270 s	1285 m	1275 m	1285 s	1285 s	C <sub>3</sub> N asymmetric	
1235 m	1203 m	1263 s	1263 sh	1235 m	1230 m	1240 m	1240 sh		
		1220 s	1230 s	1215 m	1230 m	1210 s	1213 s	(C-O + $\delta$ O-H)	
		1198 m				1190 m	1182 m		
		1170 m	1175 m					$\beta$ C-H	
1130 m	1135 m	1150 m	1145 s		1180 m	1140 m	1145 m	$\beta$ C-H, $\delta$ CD <sub>3</sub>	
				1110 w	1145 sh	1120 w			
		1115 m	1115 m		1120 m		1120 m	$\delta$ CD <sub>3</sub> sym. [N <sup>+</sup> (CD <sub>3</sub> ) <sub>3</sub> ]	

Table II .. continued

1039 w	1050 w,b	1085 m	1060 m	1050 m	1050 w	1050 w,b	$\beta_{C-H}$ ring breathing
1003 w	1025 w	1045 m	1050 sh	1000 w	1010 w	1010 w	
980 w	1003 w	1045 m	1030 m	960 m	955 m	930 m	$\gamma_{C-H}$
955 s	970 w	950 m		945 m	950 m		$\rho_{CH_3}$
945 s		935 m			945 m		
920 w	920 w,b			920 m	925 m	880 w	$\gamma_{C-H}$
880 w	875 w		890 w	900 w	900 m	855 w	
847 s	840 w	860 m	860 m	830 w	830 w	834 s	$\nu_{C_3N}$ sym.
	825 m	850 m	850 m	865 w	840 m	830 s	
			835 m	840 m	840 m		$\gamma_{C-H}, \rho_{CD_3}$
		810 m	810 sh	820 w	810 m	800 w	
			800 m	820 w	810 w		
770 s	762 s	775 s	775 s	820 w	800 m	800 w	$\gamma_{C-H}$
		765 s	765 s	750 m	780 m		
				765 m	750 m		
				745 m	740 m	750 m	$\rho_{CD_3}$
				740 m	740 m		
695 s	680 s	682 w	675 w	670 m	670 m	665 w	$\phi_{C-C}$
				670 m	670 m	665 w	$\alpha_{C-C-C}$
				675 m	670 m	640 m	
				675 w	670 m	640 m	

$\nu$  = stretching;  $\delta$  = deformation;  $\rho$  = rocking;  $\beta$  = in plane deformation,  
 $\gamma$  = out of plane deformation;  $\phi$  = out of plane ring deformation;  
 $\alpha$  = in plane ring deformation.

TABLE - III

IR BANDS OF TRIMETHYLALKYL AND  
TETRAMETHYL AMMONIUM IODIDES

Tetramethyl ammonium iodide CH <sub>3</sub> deriv CD <sub>3</sub> deriv		Trimethyl butyl ammonium iodide CH <sub>3</sub> deriv CD <sub>3</sub> deriv		Trimethyl hexyl ammonium iodide CH <sub>3</sub> deriv CD <sub>3</sub> deriv		Assignments
3080m, b						} CH <sub>3</sub> asym in N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub>
3050 m, b				3050 sh		
3010 s		3005 s		3000 s		
2950 m		2960 s	2960 s	2960 s, b	2950 s, b	} CH <sub>3</sub> sym in -N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub>
2905 m		2930 s	2930 s	2915 s	2915 s	
2870 m		2870 s	2870 s	2865 sh	2865 sh	} CH <sub>3</sub> , } CH <sub>2</sub>
2830 w		2830 sh		2850 s	2850 s	
2725 w		2730 w	2730 w	2700 w		} CD <sub>3</sub> asym.
	2300 mb		2280 sh		2260 sh	
	2265 s		2260 m		2250 s	
	2245 sh		2255 m		2240 sh	
	2170 wb		2195 w		2200 w	
	2115 w		2120 w		2120 w	
	2070 w		2095 w		2100 w	
	2070 s		2070 m		2075 m	
1480 s		1470 s	1460 s	1475 s, b	1460 s	} CH <sub>3</sub> asym. and sym. in N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub>
		1440 s	1435 s	1435 s, b	1435 s, b	
1395 s		1410 sh	1400 m	1410 s		} CH <sub>3</sub> , } CH <sub>2</sub> asym. and sym.
		1385 m	1370 m	1390 s	1390 s	
				1365 s	1360 s	} CH <sub>2</sub> wagging.
		1345 m	1345 m	1330 sh	1330 sh	
1285 m, w	1290m, w	1280 w		1270 m	1270 w	} C <sub>3</sub> N asym, } C <sub>4</sub> N asym.
	1225m, w	1275 w, b	1275 m			
		1240 m	1250 m	1245 m	1240 m	} C-N
				1225 w	1215 w	

Table III - continued

1180 s		1165 s		1160 s	$\delta$ CD <sub>3</sub> asym.
	1145 m	1145 sh	1145 m	1145 sh	CH <sub>2</sub> twist- ing.
1065 s		1120 w		1100 m	$\delta$ CD <sub>3</sub> sym.
	1100 m	1095 m	1100 w	1090 m	} C-C, $\delta$ CCC
	1060 m	1060 m	1060 m	1060 m	
	1030 m	1025 w	1000 m,w	1000 sh	
940 s		970 s		970 sh	} $\rho$ CH <sub>3</sub> in N <sup>+</sup> (CH <sub>3</sub> ) <sub>3</sub>
915 m		928 s		955 s	
		910 s		910 s	
		900 s			$\nu$ C-C
		880 m	875 m	890 m	$\nu$ C <sub>3</sub> N sym.
855 w					} $\rho$ CD <sub>3</sub> , CH <sub>2</sub>
820 s		820 m		825 sh	
805 s	800 m	805 s		815 s	
770 w					} $\rho$ CH <sub>2</sub>
			760 w	760 w	
		730 s	730 s	730 s	730 s

---

$\nu$  = stretching,  
 $\delta$  = deformation,  
 $\rho$  = rocking.

difference between the medium strong band at  $3010\text{ cm}^{-1}$  and the others is not clearly seen in the o, m, p hydroxy phenyl trimethyl ammonium iodides due to superposition of the broad hydroxyl absorption, it is very evident in phenyl, n-hexyl, n-butyl trimethyl ammonium iodides and tetramethyl ammonium iodide. Similar bands have been observed in tetramethyl ammonium halides<sup>10-13, 17,18</sup>, trimethyl ammonium iodide<sup>16</sup> ( $R = H, CH_3, C_7H_{15}$  etc.), glycine betaine<sup>14</sup> and its derivatives and ascribed to  $CH_3$  asymmetric stretching ( $3010\text{ cm}^{-1}$ ) and symmetric stretching modes ( $3000-2800\text{ cm}^{-1}$ ). Due to the possible presence of  $CH_3$  deformations overtones, it is not possible to decide which of the weak bands are due to symmetric methyl stretching modes. The shift of the asymmetric band to higher frequency is ascribed<sup>34</sup> to the charge on the nitrogen and this shift has resulted in the absence of Fermi resonance interaction between the methyl asymmetric stretching mode and the overtone of methyl asymmetric deformation modes. In contrast in compounds containing  $N(CH_3)_2$  group (see later), there are five medium strong bands at  $3000-2800\text{ cm}^{-1}$ . The above assignments are applicable to the  $CH_3$  stretching modes in the present compounds. In tetramethyl ammonium iodide, a series of additional weak bands is found in the region  $2800-2400\text{ cm}^{-1}$  ascribable to overtone and combination modes.

In the  $CD_3$  derivatives there are two medium strong bands at  $2270$  and  $2070\text{ cm}^{-1}$  along with two to three weak bands between them. While the  $2270\text{ cm}^{-1}$  band corresponds to  $3010\text{ cm}^{-1}$

( $\nu_{\text{H}}/\nu_{\text{D}} = 1.34$ ), the  $2070 \text{ cm}^{-1}$  band does not have an equivalent in  $\text{CH}_3$  stretching region. The overtone of the  $\text{CD}_3$  symmetric deformation at  $1120 \text{ cm}^{-1}$  would lie far removed from  $2070 \text{ cm}^{-1}$  for the latter to be enhanced by Fermi resonance interaction with symmetric methyl stretching modes. The only bands that could be picked for Fermi resonance interaction with the methyl ( $\text{CD}_3$ ) symmetric stretching modes near  $2070 \text{ cm}^{-1}$  are the combination of the asymmetric skeletal stretching mode at  $1270 \text{ cm}^{-1}$  and methyl  $\text{CD}_3$  rocking mode at  $800 \text{ cm}^{-1}$ . In neopentane<sup>35</sup> a strong band at  $2050 \text{ cm}^{-1}$  in the  $\text{CD}_3$  analogue which had no equivalent in the  $\text{CH}_3$  stretching region has been ascribed to Fermi resonance interaction.

#### IV c : METHYL DEFORMATION REGION

In the methyl deformation region, only two bands are observed instead of expected five bands. The two bands moving to lower frequency on  $\epsilon$ -deuteration at about  $1470$  and  $1400 \text{ cm}^{-1}$  (latter broad due to splitting in tetramethyl ammonium iodide) can be ascribed to methyl asymmetric and symmetric deformation modes respectively. The methyl deformation modes are generally found<sup>36,37</sup> at higher frequencies when methyl groups are attached to nitrogen bearing charge. Watson<sup>37</sup> has ascribed this shift to field effects. The corresponding  $\text{CD}_3$  deformation modes are at about  $1160$  and  $1100 \text{ cm}^{-1}$  except in tetramethyl ammonium iodide where they are found at  $1180$  and  $1060 \text{ cm}^{-1}$ . The  $\nu_{\text{H}}/\nu_{\text{D}}$  for these modes is about  $1.27$ . This value compared to the theoretical ratio of  $1.36$  suggests some mixing of  $\text{CD}_3$  deformation with probably

$\text{NC}_3$  stretching modes. Such coupling between  $\text{CD}_3$  deformation modes and skeletal modes has been reported<sup>38</sup>.

#### IV d : SKELETAL STRETCHING BANDS

The assignment of the skeletal stretching and methyl rocking modes in tetramethyl ammonium halides and trimethyl ammonium derivatives as mentioned in the introduction have not been satisfactorily established. It has been possible to arrive at definite conclusions and establish characteristic frequencies with regard to these modes for  $\text{N}^+(\text{CH}_3)_3$  group by a study of  $\text{CD}_3$  analogues. A band in the region  $1270\text{-}1250\text{ cm}^{-1}$  found in the spectra of all trimethyl derivatives is ascribed to  $\text{C}_3\text{N}$  asymmetric stretching mode. A stretching mode of aromatic  $\text{C-N}^+$  bond is located near  $1300\text{ cm}^{-1}$  in aryl derivatives. In alkyl trimethyl ammonium iodides, a band near  $1240\text{ cm}^{-1}$  is assigned to N-alkyl stretching mode. In the paraffins containing tertiary butyl group  $\text{R-C}(\text{CH}_3)_3$  Simpson and Sutherland<sup>3</sup> have assigned two bands in the region  $1240\text{-}1200\text{ cm}^{-1}$  to the asymmetric stretching ( $\text{C-C}_3$ ) and  $\text{R-C}$  stretching modes which coalesce into one in neopentane. Similarly, the single band at  $1280\text{ cm}^{-1}$  in tetramethyl ammonium iodide is ascribable to asymmetric  $\text{NC}_4$  stretching mode in line with Ebsworth and Sheppard<sup>10</sup>.

The symmetric  $\text{C}_3\text{N}$  stretching mode is assigned to the absorption bands between  $880$  and  $800\text{ cm}^{-1}$  in the trimethyl ammonium derivatives. In the tetramethyl ammonium iodide, this mode is IR inactive and no band is observed. A band at  $755\text{ cm}^{-1}$  (Raman spectrum) has been ascribed to  $\text{C}_4\text{N}$  symmetric stretching

mode in tetramethyl ammonium halides<sup>6,10,13,17</sup>. Bands near  $800\text{ cm}^{-1}$  have been ascribed to  $C_3N$  symmetric stretching mode in glycine betaine and its derivatives<sup>14</sup>.

#### IV e : METHYL ROCKING MODES

The expected methyl rocking modes in trimethyl ammonium derivatives are three E modes and one  $A_1$  mode. In the spectra of parent derivatives, multiple strong bands between  $970$  and  $900\text{ cm}^{-1}$  which get shifted on deuteration to  $800$ - $750\text{ cm}^{-1}$  are found which may be ascribed to three E modes of methyl rocking vibration. In alkyl trimethyl ammonium derivatives, the  $CD_3$  rocking bands are found near  $800\text{ cm}^{-1}$  ( $\nu_H/\nu_D = 1.17$ ) while in phenyl derivatives, these modes are found at  $800$ - $750\text{ cm}^{-1}$  ( $\nu_H/\nu_D = 1.17 - 1.27$ ). The complete shift of the bands at  $970$ - $900\text{ cm}^{-1}$  in the  $RN^+(CH_3)_3$  to  $800$ - $750\text{ cm}^{-1}$  in  $RN^+(CD_3)_3$  establish beyond doubt the assignment of these bands to methyl rocking modes. Less than quantitative shift ( $1.36$ ) shows the mixed nature of this mode which incorporates contributions from a C-N stretching mode. It is suggested that these strong and multiple absorption bands found in the present compounds and many others in the narrow region from  $970$ - $900\text{ cm}^{-1}$  may be used as characteristic absorption bands of the compounds containing  $-N^+(CH_3)_3$  group. This was suggested by Hume et al.<sup>16</sup>, but they had erroneously assigned these modes to  $C_3N$  skeletal stretching vibrations like many others.



Similar strong absorption bands were reported earlier<sup>10-19</sup> in the spectra of compounds containing the  $-N^+(CH_3)_3$  group. Edsall<sup>6</sup> who studied the Raman spectra of trimethyl, tetramethyl and trimethyl hydroxy ammonium ions assigned the bands near  $950\text{ cm}^{-1}$  to  $C_3N$  asymmetrical stretching by comparison with the assignments in corresponding hydrocarbons by Kohlrausch<sup>7,8</sup>. Kohlrausch argued that frequencies above  $1200\text{ cm}^{-1}$  were too high to arise from carbon skeletal vibrations. However, Edsall has pointed out that they yielded low values of force constants for neopentane and tetramethyl ammonium ion. There has been since then a tendency to assign all absorption frequencies higher than  $1100\text{ cm}^{-1}$  to hydrogen deformation modes and below  $1100$  till  $750\text{ cm}^{-1}$  to skeletal stretching absorptions. Subsequent assignments by Simpson and Sutherland<sup>2,3</sup> for comparable tertiary butyl group where bands in the region  $1250-1200\text{ cm}^{-1}$  were ascribed to skeletal modes and which give reasonable values of force constants and were later established by study of  $CD_3$  analogues<sup>5</sup>, were not taken into account in the assignment of trimethyl and tetramethyl ammonium compounds by many later workers.

Ebsworth and Sheppard<sup>10</sup> had studied the spectra of mono, di, tri and tetramethyl ammonium iodides. In the spectrum of trimethyl ammonium iodide, the bands near  $950\text{ cm}^{-1}$  and  $1250\text{ cm}^{-1}$  were assigned to  $C_3N$  asymmetric stretching and methyl rocking modes respectively. However, in tetramethyl ammonium iodide, the assignments were reversed and the bands near  $1280$

and  $950\text{ cm}^{-1}$  were assigned to asymmetric  $\text{C}_4\text{N}$  stretching and methyl rocking modes respectively. Lorenzelli and Möller<sup>11</sup>, Bottger and Geddes<sup>12</sup> and Krishnamoorthy<sup>13</sup> assigned bands near  $1280$  and  $950\text{ cm}^{-1}$  to  $\text{CH}_3$  rocking and  $\text{C}_3\text{N}$  stretching modes respectively in tetramethyl ammonium halides.

Steger and Lorenz<sup>14</sup> assigned bands near  $950$  and  $1300\text{-}1100\text{ cm}^{-1}$  to  $\text{C}_3\text{N}$  stretching and  $\text{CH}_3$  rocking modes respectively in glycine betaine and some of its derivatives. Van Senden<sup>15</sup> had analysed the IR spectra of a series of alkyl trimethyl ammonium halides  $\text{R-N}^+(\text{CH}_3)_3\text{Hal}^-$  where R varied from  $\text{CH}_3$ ,  $\text{C}_3\text{H}_7$ , etc. From the high intensity of the band at  $950\text{ cm}^{-1}$ , which he argued would be expected from the polar nature of the  $\text{C-N}^+$  bond and shift in its frequency on isotopic exchange with  $\text{N}^{15}$ , he assigned it to  $\text{C}_3\text{N}$  skeletal stretching mode. Probably, the small contribution of C-N stretching to the methyl rocking vibration is responsible for the  $5\text{-}10\text{ cm}^{-1}$  shift on replacement with  $\text{N}^{15}$ .

Hume et al.<sup>16</sup> have reported strong bands near  $950\text{ cm}^{-1}$  in a large number of compounds  $\text{R-N}(\text{CH}_3)_3^+$  where R = methyl, heptyl, cyclopropyl, etc. and ascribed them to  $\text{C}_3\text{N}$  skeletal stretching modes. They further suggested that these may be used to characterise the  $-\text{N}^+(\text{CH}_3)_3$  group in view of their strong nature and presence in a large number of compounds containing this group.

Similar assignments were maintained in two recent Raman and infrared spectral studies of tetramethyl ammonium ion by Anhouse and Tobin<sup>17</sup> and Harmon et al.<sup>18</sup>. The Raman spectral studies<sup>17</sup> in  $N^+(CH_3)_4OH^- \cdot 5H_2O$  and  $(CH_3)_4N^+I^-$  supported the assignments of Edsall<sup>6</sup> for the tetramethyl ammonium ion. Harmon et al.<sup>18</sup> have studied the effect of crystal symmetry on absorption frequencies of tetramethyl ammonium ion in compounds with various anions. They found the splitting of the band near  $950\text{ cm}^{-1}$  in agreement with its assignment to a skeletal stretching mode.

C H A P T E R - V

INFRARED SPECTRA OF NN-DIMETHYL ANILINE  
o, m AND p HYDROXY NN-DIMETHYL ANILINES  
 AND THEIR CD<sub>3</sub> ANALOGUES

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The spectra of NN-dimethyl aniline, o, m and p hydroxy NN-dimethyl anilines and their CD<sub>3</sub> analogues are presented in Figure Nos. 8 to 11.

The absorption frequencies are tabulated in Table No. IV.

V a : METHYL STRETCHING REGION

In the spectra of dimethylamino compounds, the band pattern of five medium strong absorption bands at  $\sim 2975$ , 2940, 2870, 2840 and 2800  $\text{cm}^{-1}$  is unmistakably different from that of N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub> group. In the CD<sub>3</sub> analogues the band pattern is retained except for the appearance of weaker single broad band in place of medium strong 2870 and 2840  $\text{cm}^{-1}$  bands. The exact origin of these two bands is not well understood since the number of methyl stretching modes expected is 4 due to the doubly degenerate asymmetric and symmetric vibrations. It has been suggested<sup>34</sup> that Fermi resonance interaction of the overtone of methyl deformation with CH<sub>3</sub> stretching mode is partly responsible for it. The absence of the five medium strong band

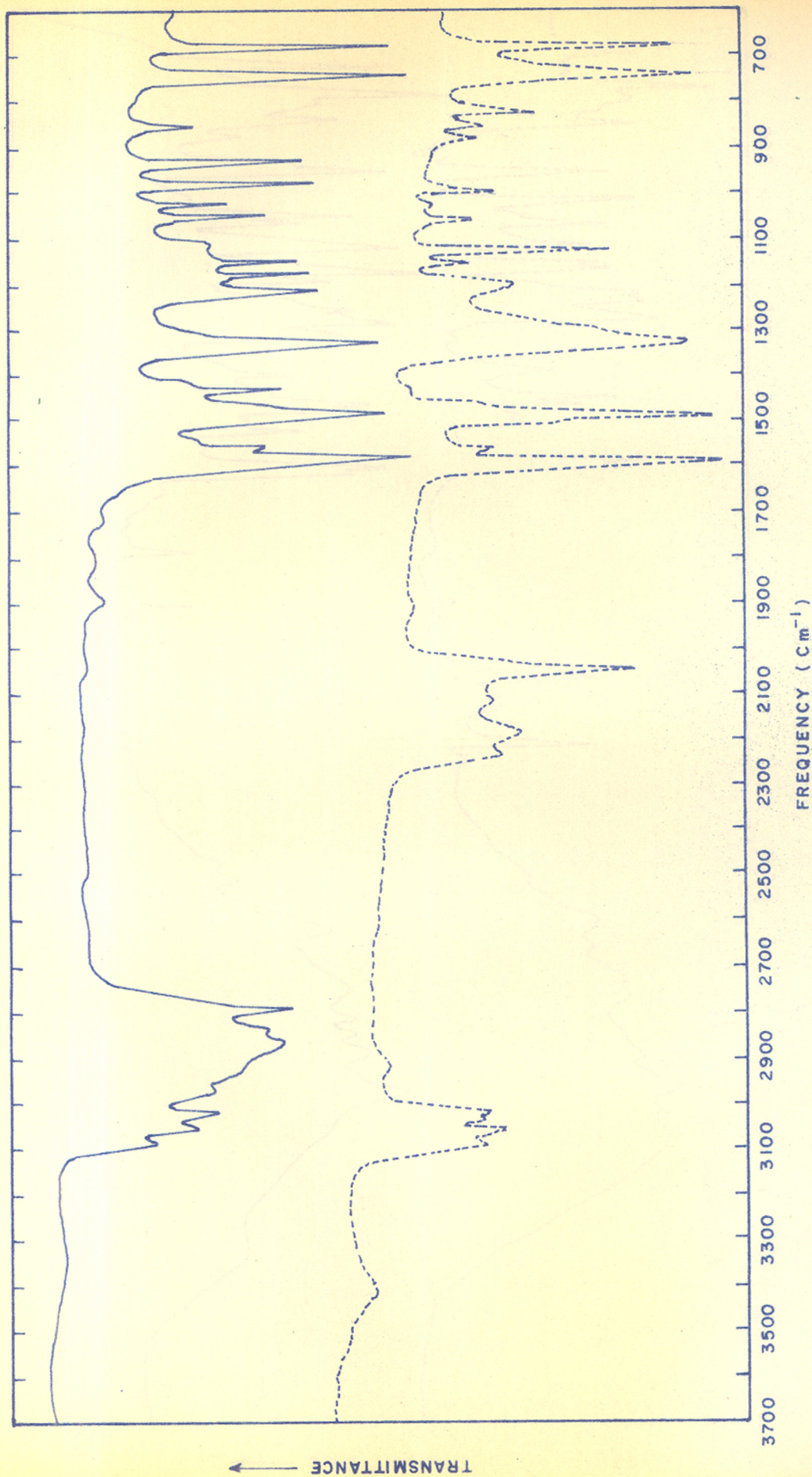


FIG. 8 . IR SPECTRA OF NN-DIMETHYL ANILINE ( — )  
 $\text{CD}_3$  ANALOGUE ( - - - )

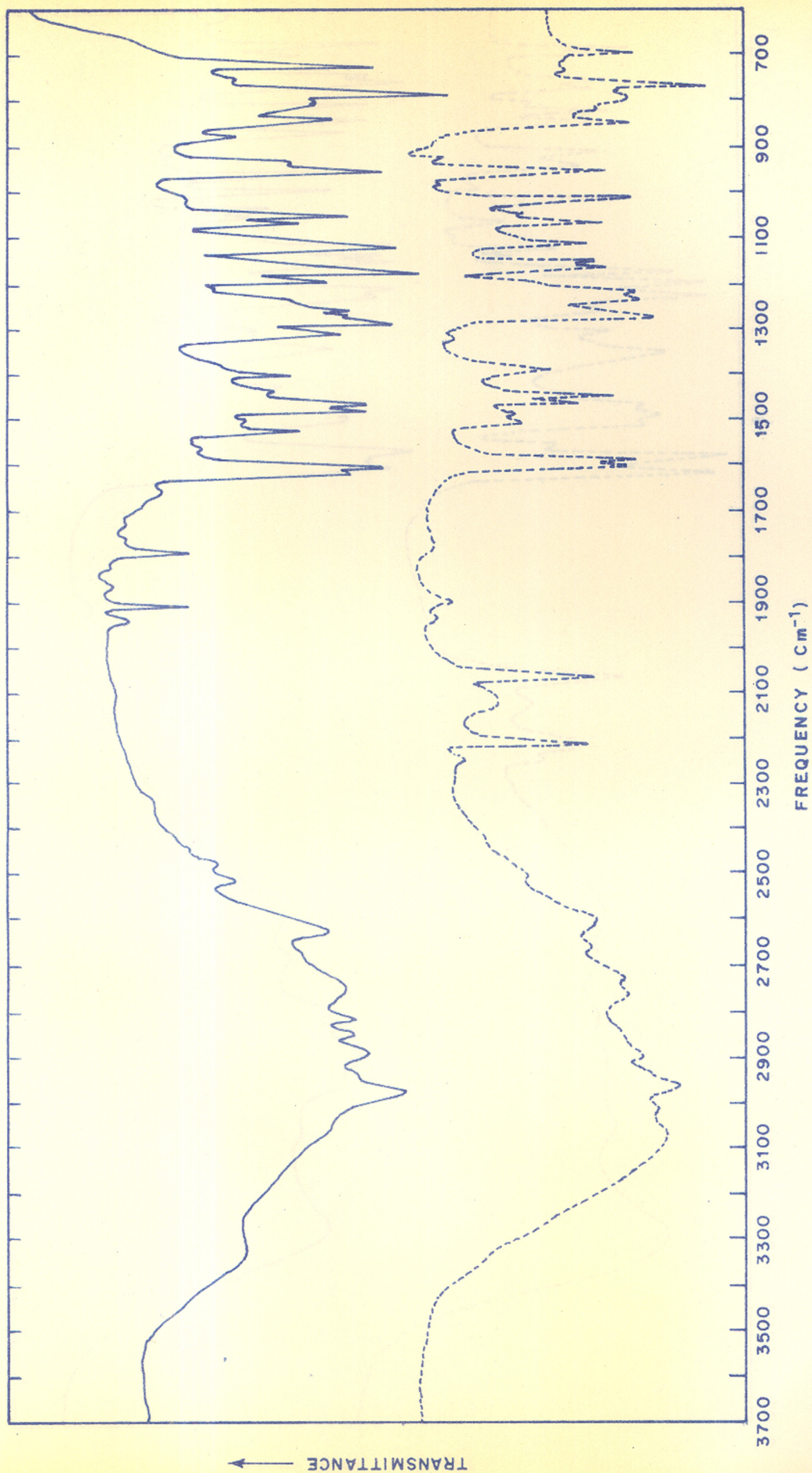


FIG. 9. IR SPECTRA OF O-HYDROXY N,N-DIMETHYL ANILINE ( — )  
 $\text{CD}_3$  ANALOGUE ( - - - )

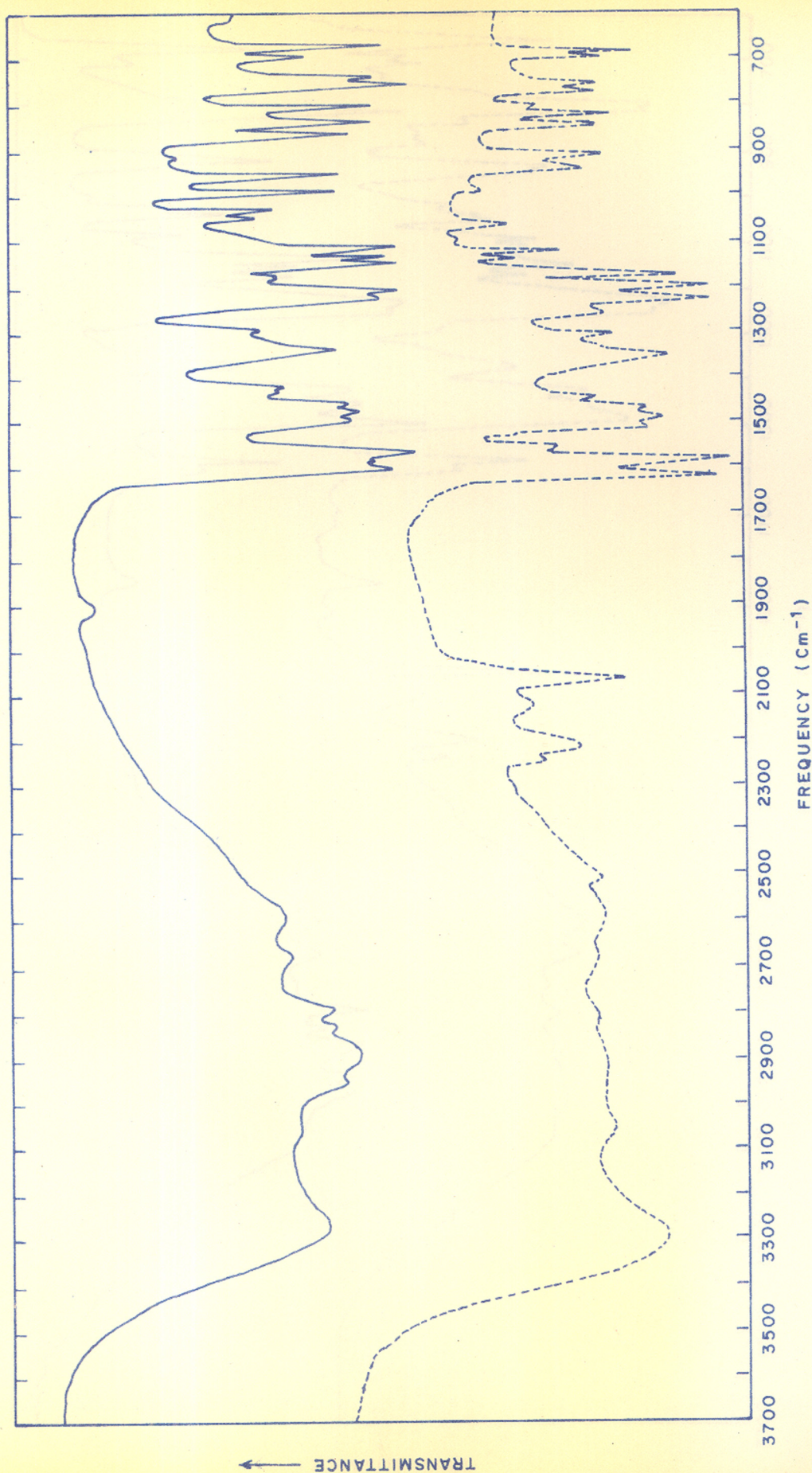


FIG. 10. IR SPECTRA OF M-HYDROXY NN-DIMETHYL ANILINE (——) AND ITS  $\text{CD}_3$  ANALOGUE (-----)

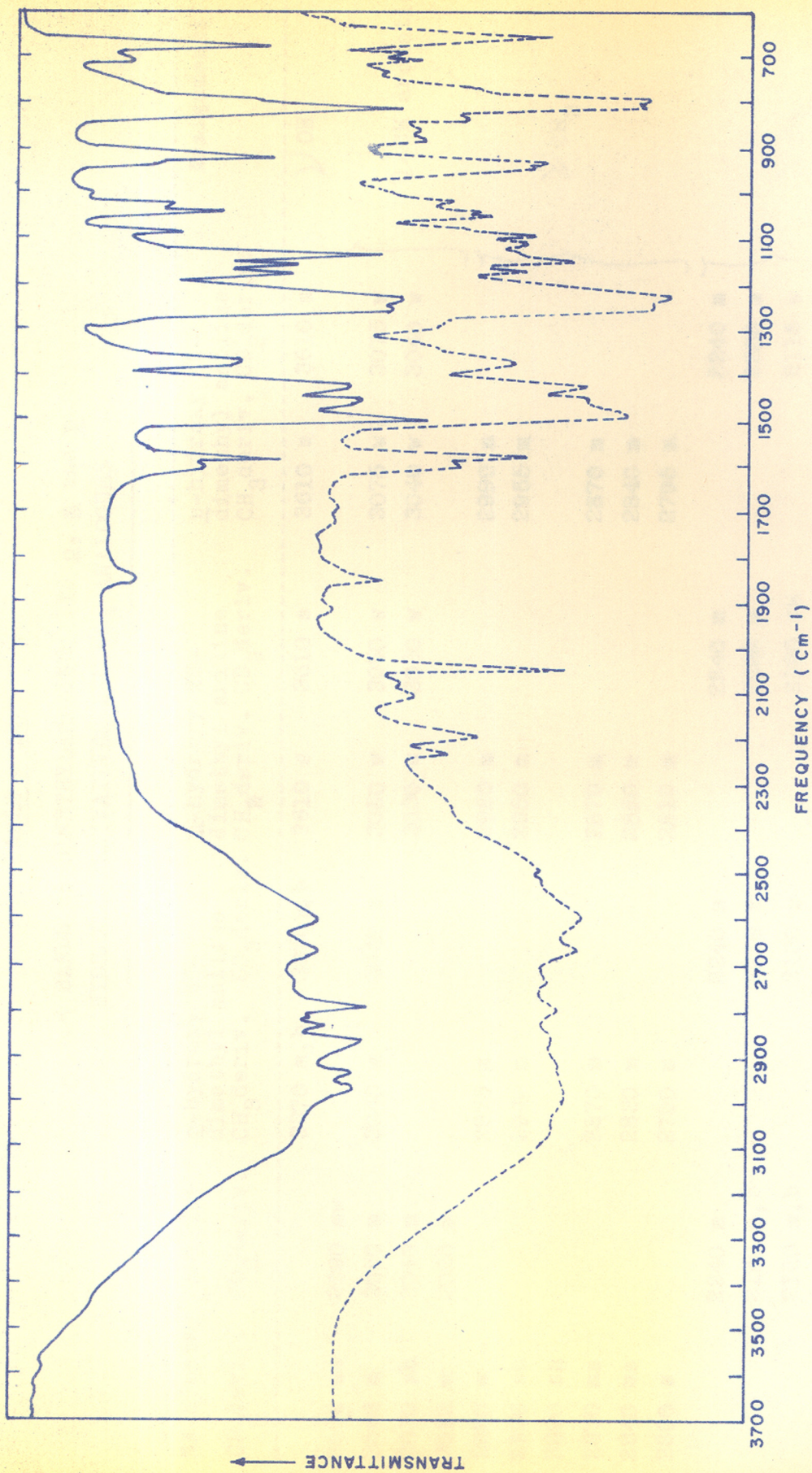


FIG. 11 . IR SPECTRA OF p-HYDROXY NN-DIMETHYL ANILINE ( ——— )  
 $\text{CD}_3$  ANALOGUE ( - - - - - )



TABLE - IV

IR BANDS OF DIMETHYLANILINE, ITS o, m and p  
HYDROXYL DERIVATIVES AND CD<sub>3</sub> ANALOGUES

	o-hydroxy NN- dimethyl aniline CH <sub>3</sub> deriv. CD <sub>3</sub> deriv.	m-hydroxy NN- dimethyl aniline CH <sub>3</sub> deriv. CD <sub>3</sub> deriv.	p-hydroxy NN- dimethyl aniline CH <sub>3</sub> deriv. CD <sub>3</sub> deriv.	Assignments
NN-dimethyl aniline CH <sub>3</sub> deriv. CD <sub>3</sub> deriv.	3370 m,b	3610 s	3610 s	OH
3090 mw	3040 m	3050 w	3075 w	} CH aromatic
3060 m	3040 m	3050 w	3075 w	
3030 sh	3040 m	3030 w	3040 w	
3020 m				
2980 m	2975 m	2980 m	2990 m	} CH <sub>3</sub>
2930 sh	2940 m	2950 m	2955 m	
2890 sh				
2870 ms	2870 m	2870 m	2870 m	} CD <sub>3</sub>
2840 ms	2830 m	2850 m	2840 m	
2800 s	2790 m	2810 m	2795 m	
2240 m	2240 m	2240 m	2240 m	
2190 m,b	2210 m	2220 m	2200 m	
2120 m,b	2130 w	2190 sh	2115 w	
	2100 w	2130 w,b	2095 w	
2055 s	2060 m	2070 m	2060 m	

Table IV ... continued

1910 bw	1910 bw	1940 w	1940 w	1860 w	1860 w	1860 w	1860 w	1740 vw	Aromatic substitution pattern.
1800 w	1800 w	1895 w	1895 w	1927 vw	1927 vw	1927 vw	1927 vw		
1600 s	1600 s	1595 m	1600 s	1620 s	1620 s	1620 s	1620 s	1610 m	C-C aromatic
1570 m	1570 m	1587 s	1585 s	1580 s	1580 s	1580 s	1580 s	1590 m	
1500 s	1500 s	1510 m	1510 m	1510 s	1510 s	1510 s	1510 s	1505 s	
		1485 m	1485 m	1490 s	1490 s	1490 s	1490 s		
1440 ms		1445 m	1445 m	1470 s	1470 s	1470 s	1470 s	1460 m	CH <sub>3</sub>
		1460 s	1440 m	1450 m	1450 m	1450 m	1440 m	1440 m	
		1380 m	1380 m	1350 s	1350 s	1350 s	1350 s	1380 m	(2) C-O + δ(O-H)
1340 s	1340 s	1290 m	1290 sh	1310 m	1310 m	1310 m	1310 m	1300 sh	C-N aromatic.
		1265 s	1270 s	1260 m	1260 m	1260 m	1260 m	1275 s	
		1250 m	1230 m	1240 s	1230 s	1230 s	1230 s	1250 s	(2) C-O + δ(O-H)
1220 ms	1205 ms	1235 m	1215 m	1220 s	1200 s	1200 s	1190 ms	1185 m	C <sub>2</sub> N asym.
1185 s	1190 m	1180 m		1185 m			1150 s		CH <sub>3</sub>
1160 m	1160 w	1160 s	1160 s	1170 s	1170 s	1170 s	1170 m	1160 m	βC-H
1130 m	1135 s	1150 sh	1150 m	1150 m	1135 m	1135 m	1120 m	1120 m	δCD <sub>3</sub> , δC-H i.p.
			1115 sh						βCH
1060 s	1060 mb	1050 m	1060 m	1060 m	1060 m	1060 m	1050 m	1055 m	
		1100 m	1105 s	1125 m	1125 m	1125 m	1695 m	1105 m	
		1050 m	1060 m	1060 m	1060 m	1060 m	1050 m	1055 m	
				1040 m	1040 m	1040 m	1040 m	1040 m	CH <sub>3</sub>

Table IV ... continued

1030 m	1020 m	1035 s	1025 m	1100 m	990 mw	1010 m	1030 m	Ring breathing.
990 s	990 m	935 s	950 s			945 m	950 ms	$\beta_{CH}$ .
940 s				970 m				$\rho_{CH_3}$ .
	900 mb	920 sh	920 m		940 m		960 sh	$\rho_{CD_3}$ .
860 m	860 w	860 m	860 sh	875 ms				} $\gamma_{C_2N \text{ sym.} + \delta_{C-H}}$
		830 m	840 m	845 ms	845 ms	830 s	825 s	
				815 ms	815 ms			
	830 m		810 m		800 w		805 s	$\rho_{CD_3}$ .
		790 m	790 m	770 m	770 m			} $\delta_{C-H}$
750 s	750 s	760 s	760 s	750 m	755 m	725 m	715 m	
	715 w			705 m	690 m	710 m	705 m	
690 s	690 s	710 s	685 s	685 s	685 m	690 m	670	$\phi_{C-C}$ aromatic.

$\delta$  = stretching;  $\delta$  = deformation;  $\rho$  = rocking;  $\beta$  = in plane deformation;

$\gamma$  = out of plane deformation;  $\phi$  = out of plane ring deformation;

$\alpha$  = in plane ring deformation.

pattern in compounds<sup>34,39-42</sup> where the lone pair on nitrogen of  $N(CH_3)_2$  group is delocalised surely establishes its involvement in the enhancement of  $CH_3$  stretching bands. The strong hydroxyl stretching absorption in solid state spectra of o, m, p hydroxy NN-dimethyl anilines near  $3000\text{ cm}^{-1}$  (shift of  $\sim 600\text{ cm}^{-1}$  from free  $\nu$  O-H band) indicates strong O-H...N hydrogen bonding and suggests absence of delocalisation of lone pair on N into the ring. The dilute solution ( $\sim 10^{-4}M$ ) spectrum of o-dimethyl amino phenol in carbon tetrachloride<sup>43,44</sup> shows  $\nu$ OH band at  $3350\text{ cm}^{-1}$  due to O-H...N intramolecular hydrogen bonding.

From a detailed study of a large number of simple compounds containing  $CD_2H$  group attached to nitrogen etc. McKean<sup>45,46</sup> has shown that in the gaseous phase, they give rise to two CH stretching modes corresponding to two conformations of the CH group with respect to the lone pair on nitrogen. The lower frequency (weaker bond) was ascribed to the trans conformation. The above assignments are unambiguous because there is no CH deformation mode, whose overtone can interact with CH stretching fundamental to complicate the bands in that region. However in the solid state spectra of the present compounds, it is not possible to assume the presence of both conformations without adequate proof from molecular structure data obtained either by X-rays or preferably from neutron diffraction measurements. In the absence of these, after

ascribing the highest frequency band to  $\text{CH}_3$  asymmetric stretching fundamental, two or three of the lower frequency bands can be ascribed to Fermi resonance interaction of the overtones of the methyl deformation mode with methyl symmetric stretching modes.

V b : METHYL DEFORMATION REGION

The band near  $1440 \text{ cm}^{-1}$  may be ascribed to methyl asymmetric/symmetric deformation mode shifting to about  $1120 \text{ cm}^{-1}$  in  $\text{CD}_3$  analogues ( $\nu_{\text{H}}/\nu_{\text{D}} = 1.28$ ). A single band instead of the expected four bands for methyl deformation mode has been reported when methyl group is attached to nitrogen. This is unlike the comparable isopropyl group where the symmetric  $\text{CH}_3$  deformation mode is characterised by a doublet near  $1350 \text{ cm}^{-1}$  along with asymmetric deformation at  $\sim 1460 \text{ cm}^{-1}$ . The low  $\nu_{\text{H}}/\nu_{\text{D}}$  (theoretical 1.33) suggests some mixing probably with the skeletal stretching mode.

V c : SKELETAL STRETCHING MODES

In the region below  $1300 \text{ cm}^{-1}$ , skeletal stretching modes and methyl rocking modes of the dimethylamino group are expected to lie. With the help of the spectra of the  $\text{CD}_3$  analogues, it has been possible to arrive at definite assignments for these modes. The band at  $1250\text{--}1185 \text{ cm}^{-1}$  which is unaffected on c-deuteration in all the compounds is ascribed to  $\text{C}_2\text{N}$  asymmetric stretching mode. This assignment is comparable to that for the isopropyl group for the band near  $1170 \text{ cm}^{-1}$  which is extensively used to identify this group<sup>1</sup>. However, a band in the region

1000-1100  $\text{cm}^{-1}$  has been ascribed to  $\text{C}_2\text{N}$  asymmetric stretching mode in dimethylaniline<sup>21</sup> (1046-  $\text{cm}^{-1}$ ), dimethylamine<sup>20,23</sup> (1024  $\text{cm}^{-1}$ ), trimethylamine<sup>47</sup> (1096  $\text{cm}^{-1}$ ) and compounds containing dimethylamino group<sup>22-24</sup> attached to an aromatic ring. Goldfarb and Khare<sup>48</sup> have assigned bands at 1270 and 1217  $\text{cm}^{-1}$  in trimethylamine and its deuterated analogue to asymmetric C-N stretching modes.

A band found in the region 860-800  $\text{cm}^{-1}$  which is also very little affected by c-deuteration in the present compounds is assigned to the corresponding symmetric stretching of the  $\text{C}_2\text{N}$  skeleton. A band near 827  $\text{cm}^{-1}$  has been ascribed to this mode in trimethylamine<sup>47,48</sup> by comparison with the spectra of the c-deuterated analogues. However, in dimethylaniline<sup>21</sup> and other compounds containing dimethylamino group<sup>22-24</sup>, a band near 940  $\text{cm}^{-1}$  has been ascribed to this mode.

V d : METHYL ROCKING MODES

A single band found near 1150  $\text{cm}^{-1}$  in place of expected two bands, shifting to 925  $\text{cm}^{-1}$  in corresponding  $\text{CD}_3$  analogues is ascribed to the methyl rocking mode of the dimethyl amino group in the present compounds. In the m-dimethylamino phenol, an additional rocking mode shifting to 800  $\text{cm}^{-1}$  in  $\text{CD}_3$  analogue was observed. In dimethyl aniline an additional band at 940  $\text{cm}^{-1}$  was also shifted on c-deuteration to 830  $\text{cm}^{-1}$  indicating some contribution from rocking mode. From the

$\nu_{\text{H}}/\nu_{\text{D}} = 1.25 - 1.29$  for the rocking mode near  $1150 \text{ cm}^{-1}$ , it can be concluded that the mixing from other modes is not large. In trimethylamine, Gayles<sup>47</sup> found bands at 1269, 1195 and  $1036 \text{ cm}^{-1}$  shifting to 937, 876,  $808 \text{ cm}^{-1}$  on c-deuteration and ascribed the former bands to  $\text{CH}_3$  rocking modes. Goldfarb and Khare<sup>48</sup> however assigned bands at 1187, 1098 and  $1037 \text{ cm}^{-1}$  to  $\text{CH}_3$  rocking modes. Two bands in the region  $1200 - 1100 \text{ cm}^{-1}$  and a band near  $1225 \text{ cm}^{-1}$  have been ascribed to<sup>22-24</sup>  $\text{CH}_3$  rocking modes in large number of compounds containing dimethylamino group.

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

The present work highlights the importance of the study of deuterated analogues in establishing the nature of vibrations even in fairly simple groups like  $-N(CH_3)_2$  and  $-N^+(CH_3)_3$ . The results further indicate that the  $-N^+(CH_3)_3$  group gives rise to strong multiple absorptions in the region  $900-950\text{ cm}^{-1}$  ascribable to  $CH_3$  rocking modes which can be used to characterise the presence of such a group in molecules. Their spectra in the methyl stretching regions, a single medium strong band at  $3010\text{ cm}^{-1}$  with 4-5 weak bands below, which on c-deuterations gave rise to two medium strong bands with 2-3 weak bands were sufficiently typical particularly in comparison with the bands due to the  $-N(CH_3)_2$  group.

In the case of the  $-N(CH_3)_2$  group, it was not possible to establish a characteristic rocking vibration because we had only aromatic dimethyl amino group and the band at  $1150-1185\text{ cm}^{-1}$  ascribed to the rocking mode was not strong enough to be clearly distinguished. However, the five medium strong bands in the  $CH_3$  region was quite typical, but valid only when the lone pair in nitrogen is localised as was found by other workers.



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