On Hydrogen Bonds Intimately Related with π-Electron Systems

By Masamichi TSUBOI

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R. S. Rasmussen et al.(1), (2) pointed out that molecules such as, enolized β-diketones and salicyl aldehyde, which are characterized by the possession of both intramolecular hydrogen bond and C=O bond conjugated with other double bonds, show C=O vibration of abnormally low frequency. They suggested that in such molecules the hydrogen bond and the conjugated double bond system (or π-electron system) are intimately related to each other, and they called such molecules "conjugated chelate system". K. Kuratani, M. Tsuboi and T. Shimanouchi(3), (4) regarded that in tropolone (an isomer of salicyl aldehyde) the O—H···O bonding is intimately related to the seven-sided π-electron system. T. Shimanouchi and S. Mizushima(5) and M. G. Evans and J. Gergely(6) showed the possibility of electron transfer along the hydrogen-bonded long chain, ···HN—C=O···HN—C=O···, in proteins. This implies that the N—H···O bondings in it are intimately related to the π-electrons of C=O's. In general, in those molecules in which hydrogen bonds cooperate with π-electron systems to form a ring or a long chain, there are indications of a specially intimate relation between the hydrogen bonds and the π-electron systems.

The purpose of this paper is to present infrared and ultraviolet evidences which indicate that in these special molecules the hydrogen nuclei of the hydrogen-bonded OH

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(1) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain. *J. Am. Chem. Soc.*, **71**, 1068 (1949).

(2) R. S. Rasmussen and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1073 (1949).

(3) K. Kuratani, M. Tsuboi and T. Shimanouchi, This Bulletin **25**, 250 (1952).

(4) M. Tsuboi, This Bulletin, **25**, 369 (1952).

(5) T. Shimanouchi and S. Mizushima, This Bulletin, **21**, 1 (1948).

(6) M. G. Evans and J. Gergely, *Biochemica et Biophysica Acta.* **3**, 188 (1949).

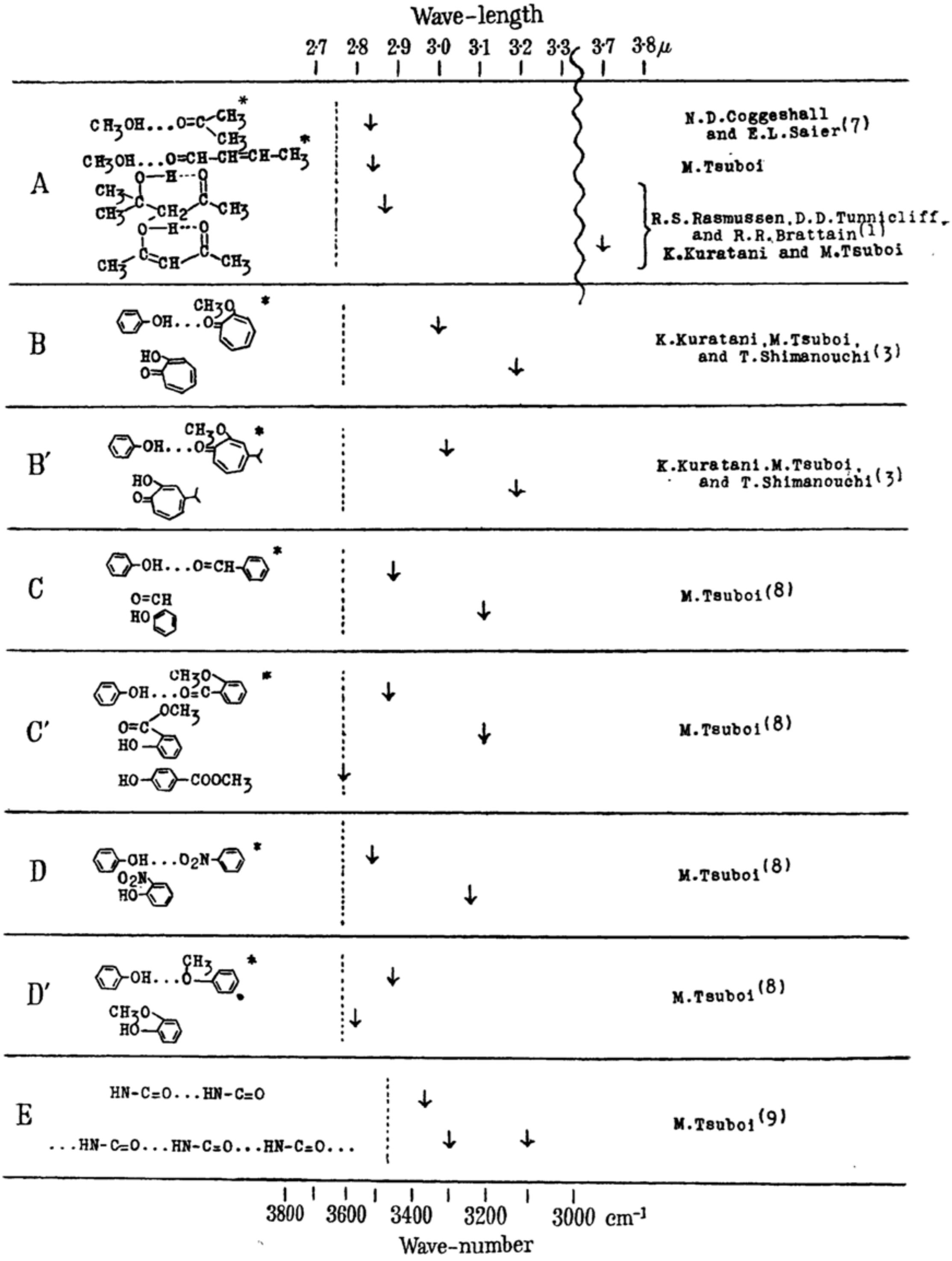

Fig. 1.

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(7) N. D. Coggeshall and E. L. Saier. *J. Am. Chem. Soc,* **73**, 5414 (1951).

(8) M. Tsuboi, This Bulletin, **25**, 60 (1952).

(9) M. Tsuboi, This Bulletin, **22**, 215, 255 (1949).

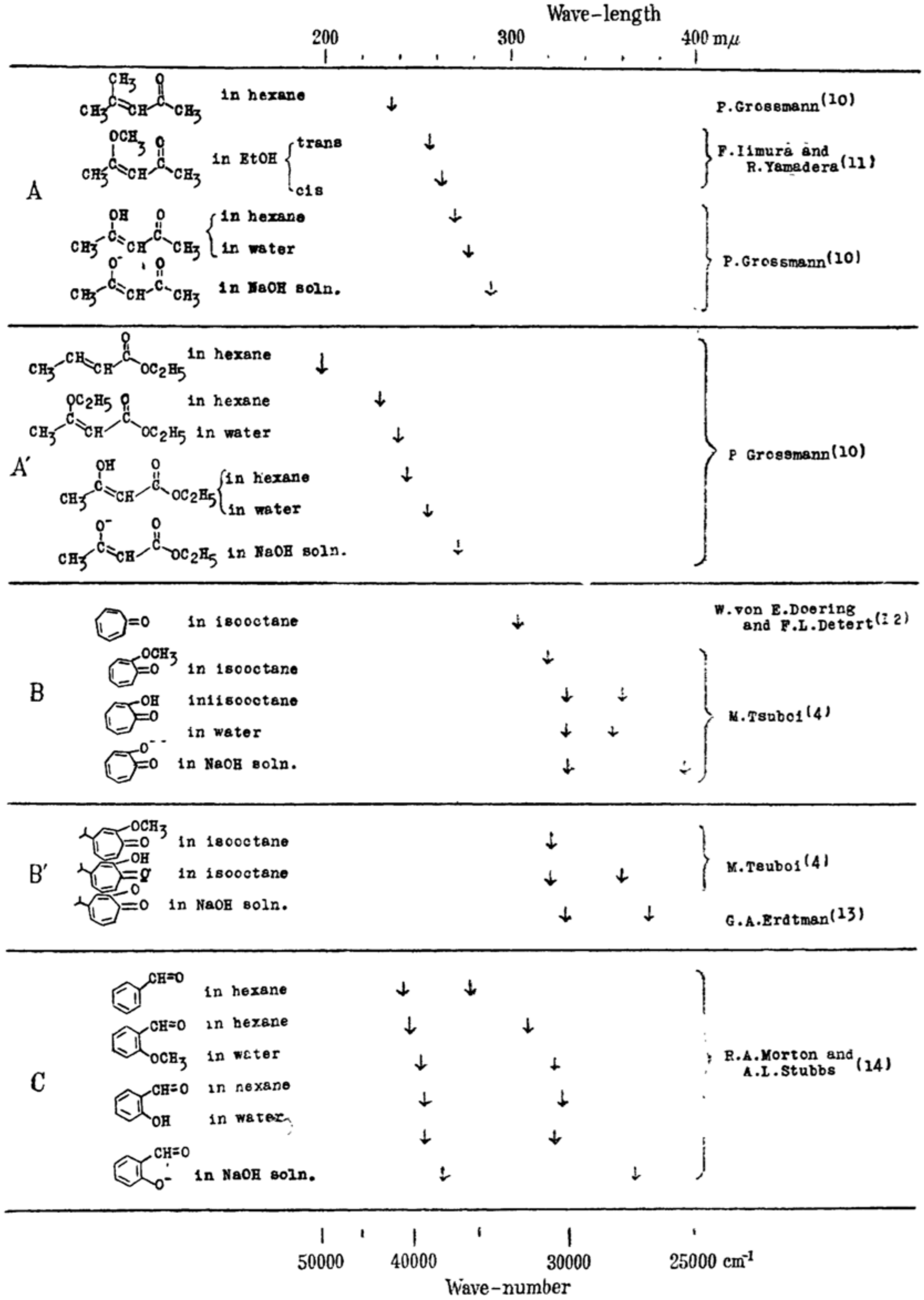

Fig. 2.

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(10) P. Grossmann, *Z. Physik. Chem.*, **109**. 305 (1924).

(11) F. Iimura and R. Yamadera. Private communications.

(12) W. von E. Doering and F. L. Detert, *J. Am. Chem. Soc.*, **73**. 876 (1951).

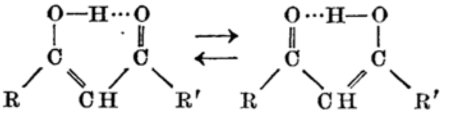
(13) G. A. Erdtman, *Acta Chemica Scandinavica*, **4**, 1031 (1950).

(14) R. A. Mortman and A. L. Stubbs. *J. Chem. Soc.*, **1940**, 1347.

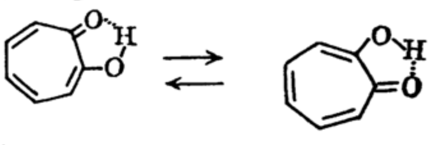
or NH groups are halfway dissociated and consequently two of the electrons of the O or N atom become partly π-electronic, having specially strong interactions with the adjacent π-electron systems, or, in other words, there occurs in these molecules a conjugation across the hydrogen bonds.

In this paper, the following five kinds of molecules are discussed. The resonance formulas tentatively given for these molecules may be considered to represent extreme cases where the relations between the hydrogen bonds and the π-electron systems are most intimate.

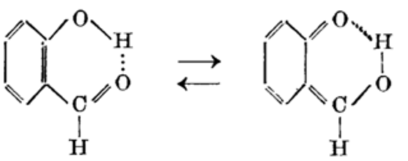
(A) Enolized β-diketones



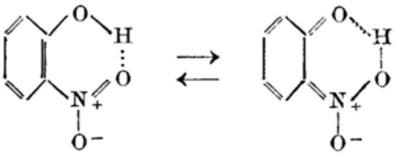
(B) Tropolone, etc.



(C) Salicyl aldehyde, etc.



(D) o-Nitrophenol



(E) Peptides

$$\cdots O{=}C{-}N{-}H\cdots O{=}C{-}N{-}H\cdots$$
$$\downarrow\uparrow$$
$$\cdots H{-}O{-}C{=}N\cdots H{-}O{-}C{=}N\cdots$$

Data

The infrared and ultraviolet data are given in Figs. 1 and 2 respectively.

Fig. 1 shows the degrees in which the O—H or N—H bonds in the above-mentioned five kinds of molecules are weakened compared with the normally hydrogen-bonded O—H or N—H bonds. The arrows in the figure indicate the positions of the infrared absorption bands due to the vibrations of O—H's and N—H's in various hydrogen-bonded states, and the dotted lines, the positions of free O—H bands of alcohol and phenol and of free N—H bands of N-methylacetamide. The formulas with * in Fig. 1 represent molecular complexes which are formed in ternary solutions composed of proton-donator (phenol, etc.), proton-acceptor (benzaldehyde, etc.), and carbon tetrachloride.(8)

From Fig. 2, it may be seen that the electronic bands of the molecules now under consideration lie halfway between those of the methyl (or ethyl) ethers and anions of these molecules. The arrows in the figure indicate the positions of the ultraviolet absorption bands of several conjugated double bond systems with carbonyl groups. All of these bands, being too strong in intensity ($\varepsilon \doteqdot 10^4$) to be assigned to the transitions of $N \rightarrow E_n$ type,(15) may be assigned to those of $N \rightarrow V_n$ type.(15)

Discussions

A. Enolized β-diketones. (Cf. Figs. 1A, 2A and 2A′) — The O—H band of enolized acetylacetone is diffuse, broad, and weak, and is situated at a position (3.7 μ), much displaced from the proper position of O—H (2.75 μ). On the other hand, the O—H bands in ordinary O—H···O=C bondings are rather sharp and strong, and are situated at about 2.85 μ. These facts reveal that the O—H bond in enolized acetylacetone (one of the conjugated chelate systems) is weaker than the O—H bonds in the normal O—H···O=C bondings. (The force constant of the former is as small as 60% of that of the latter).

The so-called $N \rightarrow V_1$ band(15) of enolized acetylacetone methyl ether, a compound in which the OCH_3 group replaces the CH_3 group in mesityloxyde, is situated at 260 mμ the position shifted as much as 25 mμ from that of the corresponding band of mesityloxyde (235 mμ)(16). The $N \rightarrow V_1$ band shifts further to about 270 mμ when the OH group replaces the OCH_3 group in enolized acetylacetone methyl ether to form enolized acetylacetone. The shifting of electronic bands due to mere $OCH_3 \rightarrow OH$ replacement being usually not so great (for instance anisole and phenol give their electronic bands almost at the same positions in nonpolar solvents), the above-mentioned shift of the $N \rightarrow V_1$ band may be something special in electronic structure. It is noteworthy in connection with this that the

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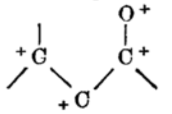
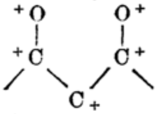
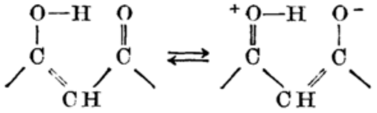
(15) H. L. McMurry, *J. Chem. Phys.*, **9**, 231, 241 (1941).

(16) This shift may be due to the electron migration from the OCH_3 toward the π-electron system of the enolized acetylacetone methyl ether. See K. F. Herzfeld, *Chem. Rev.*, **41**, 233 (1947); H. Baba and S. Nagakura, *J. Chem. Soc. Japan*, **72**, 72, 74 (1951).

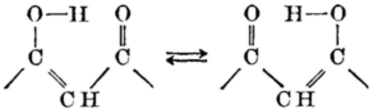
$N \rightarrow V_1$ band of enolized acetylacetone is situated at an intermediate position between the bands of its methyl ether and its anion. This fact shows that the enolized acetylacetone is intermediate in the electronic state between its methyl ether and its anion; its methyl ether being composed of the field  and four π-electrons, and its anion composed of the field  and six π-electrons (see Appendix).

R. S. Rasmussen et al⁽¹⁾ assumed a resonance:



I

to occur in enolized acetylacetone. No evidence is contradictory to this theory, but the present writer is inclined to attach importance to the resonance:



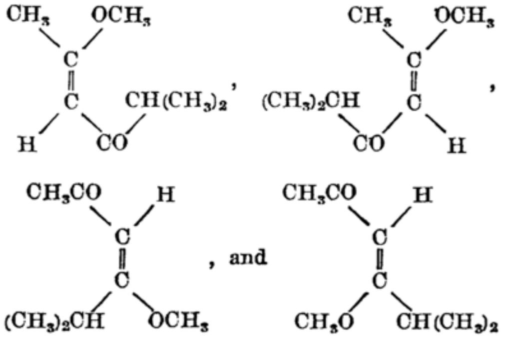
II

Thus, in the writer's view, the hydrogen atom is situated on the perpendicular bisector of the line connecting the two oxygen atoms, and the molecule has a symmetry plane which involves the bisector and is perpendicular to the molecular plane. Facts which favour the preference of resonance II rather than resonance I are:

(i) The observed dipole moment of enolized acetylacetone (about 3 D. U.) is much smaller than it should be if resonance I were predominant.⁽¹⁷⁾

(ii) Infrared absorption band due to the O—H stretching vibration of this molecule is abnormally weak in intensity.

(iii) $CH_3C(OCH_3){=}CH{-}CO{-}CH(CH_3)_2$ has four isomers,



while $CH_3C(OH){=}CH{-}CO{-}CH(CH_3)_2$ has only one⁽¹¹⁾.

B. Tropolone, etc. (Cf. Fig. 1B, 1B′, 2B and 2B′) — Phenol-tropolone methyl ether, a complex with *inter*-molecular O—H···O=C bonding, gives its O—H band at 3.00 μ. Here, the carbonyl O of O—H···O=C bonding is considered to be situated on the prolongation of the line representing the O—H bond vector. On the other hand in tropolone, with *intra*-molecular O—H···O=C bonding, the position of the carbonyl oxygen atom deviates greatly from the prolongation of the O—H bond vector line. Merely from molecular geometrical considerations, the above facts might appear to show that the intramolecular O—H···O=C bonding of tropolone must be much weaker than the intermolecular O—H···O=C bonding between phenol and tropolone methyl ether, and accordingly that the O—H band must be situated at much shorter wave-length than 3.00 μ. However, the actually observed O—H band of tropolone in carbon tetrachloride is situated at 3.19 μ, much longer wavelength than 3.00 μ, and is weaker and broader than the above 3.00 μ band⁽³⁾. This is an indication that the O—H bond in tropolone is weakened under a special circumstance due to the intimate relation between the O—H···O bonding and the conjugated double bonds in the seven-membered ring.

The ultraviolet absorption spectrum of tropolone exhibits features intermediate between those of tropolone methyl ether and tropolone anion. This may be taken as indicating that the intramolecular hydrogen bonding in tropolone gives an effect upon tropone ring to transform its electronic structure halfway toward that of tropolone anion.

As may be seen from Fig. 1B′ and 2B′ the O—H···O bonding in hinokitiol is the same in nature as that of tropolone.

C. Salicyl aldehyde, etc. (Cf. Fig. 1C, 1C′, and 2C)—The O—H bands of salicyl aldehyde and methyl salicylate are situated

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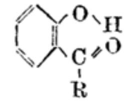
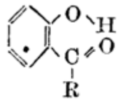
(17) According to J. B. Conant and A. F. Thompson (*J. Am. Chem. Soc.*, **54**, 4039 (1932)), keto-enol equilibrium in β-diketones shifts toward keto-form in polar solvents, and toward enol-form in nonpolar solvents, indicating that the enol-form of β-diketones is in general less polar than the keto-form. According to C. T. Zahn (*Physik. Z.*, **34**, 570 (1933)) the mean dipole moment of acetylacetone molecule is 3 D. U. in gas phase, where more than 90% of molecules take the enol-form.

at longer wave-lengths respectively than those of intermolecular complexes: phenol-benzaldehyde and phenol—methyl benzoate. This fact shows that the O—H bond in salicyl aldehyde and methyl salicylate are weakened by the intimate relations between the O—H···O bondings and the conjugated double bond systems in these molecules.

Each of the ultraviolet absorption bands of salicyl aldehyde is intermediate in its position between the corresponding bands of its methyl ether and its anion.

A. E. Martin(18) found that in  type molecules a broad O—H band is associated with the structure where R is H or CH_3, but a sharp band is produced when R is OH or OCH_3. As is known, the OH and OCH_3 groups are lower in ionization potential than the alkyl groups(19). Then, what Martin found may be expressed as follows: the relation between the hydrogen bond and the conjugated double bond system in  type molecules becomes less intimate as the ionization potential of R becomes lower.

D. *o*-Nitrophenol. (Cf. Fig. 1D and 1D′) —The shifting of the O—H band of phenol due to its forming an intermolecular hydrogen bond with nitrobenzene is only from 2.77 μ to 2.84 μ. From this it is seen that the oxygen atom of nitro group attached to the benzene ring is not a strong proton acceptor. Nevertheless, the O—H band of *o*-nitrophenol is situated at 3.08 μ, a much displaced position. Then, the intramolecular hydrogen bond in *o*-nitrophenol must also be related intimately with the π-electron system*.

E. Peptides. (Cf. Fig. 1E)—The dimer of N-methylacetamide with a single N—H···O=C bonding gives one N—H association bands at 2.97 μ, while its *long* chain polymer gives two N—H association bands at 3.03 μ and 3.22 μ(9). This fact is considered to have some connections with the view advanced by T. Shimanouchi and S. Mizushima(5) as well as by M. G. Evans and J. Gergely(6), that a "conjugation"(20) is possible along the hydrogen-bonded long chain, ···HN—C=O···HN—C=O···, in protein.

The appearance of the second N—H band at 3.22 μ is characteristic of this system. Recently, I. Oshida and Y. Oshika,(21) showed theoretically that, if in a hydrogen bond, X—H···Y, there are two almost equally stable positions of the proton between the two atoms X and Y, and if the potential barriers between these two stable positions are of certain appropriate height (Fig. 3, A), there must occur two bands in the 3 μ region from this system.

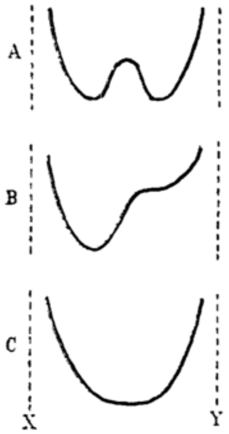
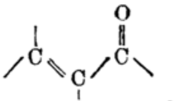
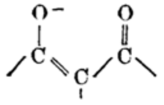


Fig. 3.—Three types (A, B and C) of the potential curve of proton in X—H···Y bonding.

It is possible that the two N—H bands of the N—H···O bondings in the long chain, ···HN—C=O···HN—C=O···, and in the ring dimers of δ-valerolactam(9),(22), ε-caprolactam(9) and diketopiperazine(9) correspond to the theoretically expected bands. Further, it is possible that in ordinary hydrogen bonds one of the potential valley is much deeper than the other (Fig. 3, B) and in the conjugated chelate system there is only one wide potential valley near the centre of the line connecting X and Y atoms (Fig. 3, C).

Appendix

Electronic states of acrolein type molecule  and enolized acetylacetone anion type molecule  will be

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(18) A. E. Martin, *Nature*, **166**, 474 (1950).

(19) A. L. Sklar, *J. Chem. Phys.*, **7**, 984 (1939).

(20) H. C. Longuet-Higgins and G. W. Wheland, *Annual Rev. Phys. Chem.*, **1**, 133 (1949).

* The O-H band due to the intramolecular hydrogen bond not related with the π-electron system is situated at a position not much displaced from 2.77μ, as is exemplified by guaiacol which gives an O-H band at 2.80μ (Cf. Fig. 1 D,).

(21) I. Oshida and Y. Oshika, *Busseiron Kenkyu*, **46**, 95 (1952).

(22) M. Tsuboi, This Bulletin, **24**, 75 (1951).

treated here according to the simple molecular orbital methods.

(I) Treatment by the LCAO Method.—Neglecting the overlap integrals, we can write the secular equation for the approximate molecular orbitals, which may be expressed as linear combinations of $2p\pi$ atomic orbitals of the C and O atoms composing these molecules, in the form:

$$\begin{vmatrix} \alpha_O-E & \gamma_{CO} & 0 & 0 \\ \gamma_{CO} & \alpha_C-E & \gamma_{CC} & 0 \\ 0 & \gamma_{CC} & \alpha_C-E & \gamma_{CC} \\ 0 & 0 & \gamma_{CC} & \alpha_C-E \end{vmatrix} = 0 \text{(acrolein)},$$

$$\begin{vmatrix} \alpha_O-E' & \gamma_{CO} & 0 & 0 & 0 \\ \gamma_{CO} & \alpha_C-E' & \gamma_{CC} & 0 & 0 \\ 0 & \gamma_{CC} & \alpha_C-E' & \gamma_{CC} & 0 \\ 0 & 0 & \gamma_{CC} & \alpha_C-E' & \gamma_{CO} \\ 0 & 0 & 0 & \gamma_{CO} & \alpha_O-E' \end{vmatrix} = 0$$

(enolized acetylacetone anion)

where α_C and α_O are the Coulomb terms for the C and O atoms, and γ_{CC} and γ_{CO} are the resonance integrals of the adjacent C—C and C—O respectively. If we assume, according to M. J. S. Dewar,(23) that

$$\alpha_C-\alpha_O=\beta$$
$$\gamma_{CO}=\sqrt{2}\,\beta$$
$$\gamma_{CC}=\beta \qquad \beta=-73.2\ \text{kcal./mol.}\ (25600\ \text{cm.}^{-1}),$$

we obtain the following values for energy levels of the π-electrons:

$$E=\alpha_C-2.22\,\beta,\ \alpha_C-\beta,\ \alpha_C+0.45\,\beta,\ \alpha_C+1.67\,\beta\ \text{(acrolein)}$$
$$E'=\alpha_C-2.34\,\beta,\ \alpha_C-2\,\beta,\ \alpha_C-0.47\,\beta,\ \alpha_C+\beta,\ \alpha_C+1.81\,\beta$$

(enolized acetylacetone anion).

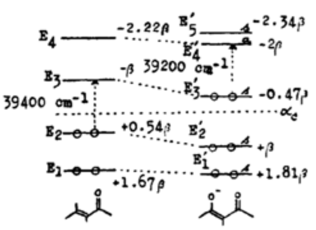
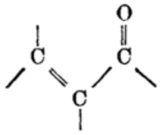


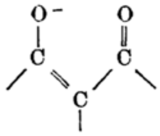
Fig. 4.

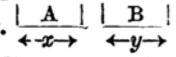
These energy levels are shown graphically in Fig. 4, in which *s* or *a* designates whether the wave function belonging to the level is symmetrical or antisymmetrical with respect to the symmetry plane of enolized acetylacetone anion molecule, which is perpendicular to the molecular plane. The observed 235 mμ (42600 cm.$^{-1}$) band of mesityloxyde may correspond to the $E_2 \rightarrow E_3$ transition (See Fig. 4, calculated 39400 cm.$^{-1}$), and the observed 290 mμ (34500 cm.$^{-1}$) band of enolized acetylacetone anion to the $E_3' \rightarrow E_4'$ transition (See Fig. 4, calculated 39200 cm.$^{-1}$).

(II) Treatment by the Free Electron Model Method.—The method assumes a model where the π-electrons in the systems



and



are one-dimensional electron-gases in the fields, A and B, of uniform potential, whose lengths are x and y respectively. 

The solution(24) of the Schrödinger equation for this model gives the energy levels shown in Fig. 5, and based on this, the wave-numbers of the $N \rightarrow V_1$ bands of acrolein and enolized acetylacetone anion should be

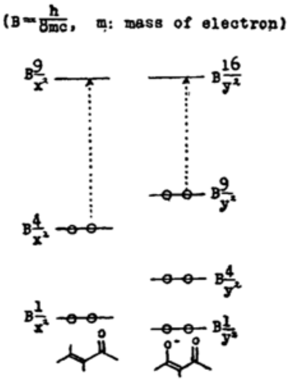


Fig. 5.

$$\nu_1=B\frac{5}{x^2} \quad \text{and} \quad \nu'_1=B\frac{7}{y^2}$$

respectively. If we put here

$$\frac{x}{y} \doteq \frac{3}{4}$$

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(23) M. J. S. Dewar, *J. Chem. Soc.*, **1950**, 2329.

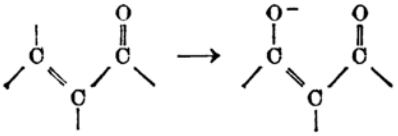
(24) N. S. Bayliss, *J. Chem. Phys.*, **16**, 287 (1948).

then
$$\frac{\nu_1}{\nu_1'} \doteqdot \frac{5}{4}$$

This is in agreement with the observed ratio,

$$\frac{\nu_{obs.}}{\nu'_{obs.}} = \frac{42600\ \text{cm.}^{-1}}{34500\ \text{cm.}^{-1}} \doteqdot \frac{5}{4}.$$

This agreement shows that the magnitude of red-shift of the $N \rightarrow V_1$ band due to the change:



may be well explained on the basis of the free electron model.

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