HYDROGEN BONDING IN AMIDES
(Electrostatic Interaction and Resonance)

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Received April 7, 1962

(Communicated by Dr. R. K. Asundi, F.A.Sc.)

I. INTRODUCTION

The functional groups responsible for the intermolecular associations in amides are the amino and carbonyl linkages, giving rise to hydrogen bonding of the type N–H–––C. The authors\textsuperscript{1, 2} have studied the intermolecular associations in primary amides and assigned the vibrational frequencies of the free and bonded N–H linkages. In the infra-red spectra of formamide and acetamide, a band in the region of 3200 cm\textsuperscript{-1} is assigned to the N–H symmetric stretching vibrations of the associated molecules and a peak at about 3430 cm\textsuperscript{-1} to that of the same mode of vibration of the free N–H linkage. In the present work, the shift in the N–H symmetric stretching frequency, due to hydrogen bond formation, has been calculated and the results are compared with those of the recorded values in formamide and acetamide. Coggeshall\textsuperscript{3} has calculated the shift in the free hydroxyl frequency of methanol due to hydrogen bonding, taking the reduction in the ionic character of the hydroxyl bond into consideration. The difference between the calculated and the recorded values by this author is 45 cm\textsuperscript{-1} which appears to be considerable.

II. STRETCHING FREQUENCY OF THE N–H GROUP AND THE DISSOCIATION ENERGY

The N–H stretching frequency is considered—as a first approximation—to be independent of the rest of the molecule. As a result of hydrogen bonding, the N–H group is immersed in a constant electric field in the presence of oxygen atom of the carbonyl group of another molecule. The Schroedinger equation for such a system with a Morse Potential function is

\[
\frac{d^2\psi}{dx^2} + \frac{8\pi^2\hbar^2}{M}\left[\frac{\psi}{E - D (1 - e^{-ax})^2}\right] \psi = 0
\]  

(1)
Hydrogen Bonding in Amides

where $M$ is the reduced mass of the N—H group and $D$ is the dissociation energy. The eigenvalues of the equation are given by

$$E(v) = \frac{a \hbar}{\pi} \left( \frac{D}{2M} \right)^{1/8} (v + \frac{1}{2}) - \frac{a^2 \hbar^2}{8\pi^2 M} (v + \frac{1}{2})^2$$

(2)

where ‘$a$’ is a constant and ‘$v$’ is the vibrational quantum number and the frequency in cm$^{-1}$ arising out of the transition from the ground level to the next vibrational level is given by

$$v = \frac{a}{\pi c} \left( \frac{D}{2M} \right)^{1/2} - \frac{a^2 \hbar}{4\pi^2 Mc}$$

(3)

where $c$ is the velocity of light.

The dissociation energy of the free N—H linkage$^4$ $D = 93.4$ Kcal./mole or $6.512 \times 10^{-12}$ erg/molecule and $M$ for the N—H group is $1.573 \times 10^{-24}$ grams. With these values of $D$, $M$ along with the free N—H stretching frequency of formamide and acetamide inserted in (3) the constant ‘$a$’ is calculated for the two amides. These values for formamide and acetamide are $2.402 \times 10^8$ and $2.40 \times 10^8$ (in cm$^{-1}$) respectively.

### III. Evaluation of Unbalanced Charges

The bond lengths and the N—H—O distances in formamide$^6$ and acetamide$^6$ are given in Table I.

**Table I**

*Bond lengths in amides in Å*

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length</th>
<th>Bond</th>
<th>Bond length</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—H</td>
<td>1.094</td>
<td>C—CH$_3$</td>
<td>1.51</td>
</tr>
<tr>
<td>C=O</td>
<td>1.243</td>
<td>C=O</td>
<td>1.28</td>
</tr>
<tr>
<td>C—N</td>
<td>1.343</td>
<td>C—N</td>
<td>1.38</td>
</tr>
<tr>
<td>N—H</td>
<td>0.995</td>
<td>N—H</td>
<td>1.00</td>
</tr>
<tr>
<td>N—H—O</td>
<td>2.930</td>
<td>N—H—O</td>
<td>2.86</td>
</tr>
</tbody>
</table>

The bond moments of various linkages$^7$—$^9$ are

- $\mu (C—H) = \mu (C—CH$_3$) = \mu (C—N) = 0.4$ D, $\mu (C=O) = 2.4$ D,
- $\mu (N—H) = 1.3$ D, $\mu (C=O) = 0.9$ D, $\mu (C—N) = 0.66$ D.
The unbalanced charges in various atoms in the two amide molecules under investigation where X is H or CH₃ are represented in Fig. 1. The unbalanced charges are calculated by the relation \( \mu = qd \), where \( \mu \) is the dipole moment of the bond, \( q \) the unbalanced charge and \( d \) the internuclear distance. \( q_1, q_4, q_5 \) and \( q_2 - q_3 \) are directly obtained from the equation \( \mu = qd \) and these results are combined with the equation \( 2q_1 + q_2 + q_3 + q_4 + q_5 = 0 \) to obtain the values of \( q_2 \) and \( q_3 \). These values are given in Table II.

IV. THE IONIC CHARACTER OF THE BONDED N–H LINKAGE

Using the known bond energies of N–N, H–H and N–H bonds in Pauling's Postulate of Additivity of Normal Covalent Bonds⁴ the energy of the N–H bond due to ionic character ‘\( \Delta \)’ is obtained as 22·1 Kcal./mole as per equation⁴

\[
\Delta = D(N–H) - \frac{1}{2} \{ D(N–N) + D(H–H) \}.
\]

\( D(N–H), D(N–N) \) and \( D(H–H) \) are the bond energies of the N–H, N–N and H–H linkages respectively. In the amides, the hydrogen atom of the amino group of one molecule is attracted by the oxygen atom of the carbonyl linkage of another molecule as indicated in Fig. 2.

The hydrogen bonding has the effect of reducing the electrostatic attraction due to the charge inequality within the N–H bond. A consequence of this is the reduction of the ionic character of the N–H bond, its dissociation energy and hence a reduction in the stretching frequency as per (3). The decrease in the stretching frequency is therefore obtained by calculating the decrease in the dissociation energy of the N–H linkage.

The fractional reduction in the ionic character of the N–H bond is given as the ratio of the electrostatic force \( F_1 \) on the hydrogen atom due to
the hydrogen bonding, to that of $F_2$ due to charge inequality in the N–H group. From $F_1/F_2 = 0.78$, the dissociation energy of the bonded N–H linkage in formamide is obtained as

$$D' = 93.4 - 22.1 \times 0.78 = 76.2 \text{ Kcal./mole}$$

or $5.31 \times 10^{-12} \text{ erg/molecule}$. The value of $D'$ for acetamide $= 5.21 \times 10^{-12} \text{ erg/molecule}$. These are used in (3) and the bonded N–H symmetric stretching frequencies in formamide and acetamide are calculated and are given in Table III. It is seen from these observations that the difference between the observed and calculated values of the frequency for the bonded N–H symmetric stretching vibrations in both the amides is of the order of 120 cm$^{-1}$.

V. EFFECT OF RESONANCE STRUCTURES

The large differences in the observed and the calculated frequencies are due to the fact that in amides, there are two resonance structures as indicated in Fig. 3.

These two structures are not equivalent. The C–N bond in amides has considerable amount of double bond character and C=O bond has a considerable amount of single bond character. To obtain the percentage of double bond character of C–N and C=O, we use the expression for the potential energy from Pauling. The potential energy

$$V(R) = \frac{1}{2} (1 - x) K_1 (R - R_1)^2 + \frac{1}{2} K_2 x (R - R_2)^2$$

(5)

$R$ is the actual bond length, $R_1$ and $R_2$ are the internuclear distances and $K_1$ and $K_2$ are the force constants for the single and double bonds respectively and $x$ is the double bond character. On differentiating with respect to $R$ and equating it to zero we have

$$(1 - x) K_1 (R - R_1) + K_2 x (R - R_2) = 0.$$  

(6)

We use the idealised single and double bond-length data from Pauling and Stewart for $R_1 (C–O) = 1.43$, $R_2 (C=O) = 1.22$, $R_1 (C–N) = 1.47$.
and $R_2 (C=\text{N}) = 1.26 \text{Å}$. When the formal charge-correction is made these bond-lengths become $R_1 (C\text{--O}) = 1.46$, $R_2 (C=\text{O}) = 1.22$, $R_1 (C\text{--N}) = 1.47$ and $R_2 (C=\text{N}) = 1.235 \text{Å}$. Using the idealised bond-length data and Badger’s equation, which is 
\[ K^{-1/3} = a_{ij} (R - b_{ij}) \] 
the force constants are calculated which are $K_1 (C\text{--O}) = 0.442$, $K_2 (C=\text{O}) = 1.185$, $K_1 (C\text{--N}) = 0.376$ and $K_2 (C=\text{N}) = 0.957$ in mega dynes/cm. The force constants and the bond-lengths, obtained after making the formal charge-corrections, are used in (6) to evaluate the double bond character $x$ of C--N and C=O in formamide and acetamide. They are 31% and 78% in formamide and 19% and 53% in acetamide respectively.

On the basis of the resonance structure B, the unbalanced charges $q_2'$, $q_3'$ and $q_5'$ on the nitrogen, carbon and oxygen atoms are different from those in structure A, while the other unbalanced charges have same values in both the structures. With $\mu (C\text{--O}) = 0.9 \text{D}$, $\mu (C=\text{N}) = 0.66 \text{D}$, $q_5'$ and $(q_2'-q_3')$ are obtained from the equation $\mu = qd$ and these are combined with $2q_1 + q_2' + q_3' + q_4 + q_5' = 0$ to give $q_2'$ and $q_3'$. In formamide $q_2' = -1.37 \times 10^{-10}$, $q_3' = -0.88 \times 10^{-10}$ and $q_5' = -0.72 \times 10^{-10}$ and in acetamide $q_2' = -1.32 \times 10^{-10}$, $q_3' = -0.85 \times 10^{-10}$ and $q_5' = -0.72 \times 10^{-10}$ in e.s.u. Then the actual unbalanced charge on nitrogen in formamide is given by $(q_2 \times 0.69 + q_2' \times 0.31)$ and that on oxygen by $(q_5 \times 0.78 + q_5' \times 0.22)$. The corresponding unbalanced charges in acetamide are $(q_2 \times 0.81 + q_2' \times 0.19)$ and $(q_5 \times 0.53 + q_5' \times 0.47)$ respectively. These values are given in Table II.

### Table II

Unbalanced charges on various atoms in amides (in $10^{-10}$ e.s.u.)

<table>
<thead>
<tr>
<th>Charge</th>
<th>Formamide</th>
<th></th>
<th>Acetamide</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without resonance</td>
<td>With resonance</td>
<td>Without resonance</td>
<td>With resonance</td>
</tr>
<tr>
<td>$q_1$</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>$q_2$</td>
<td>-0.67</td>
<td>-0.88</td>
<td>-0.64</td>
<td>-0.77</td>
</tr>
<tr>
<td>$q_3$</td>
<td>-0.37</td>
<td>-0.53</td>
<td>-0.35</td>
<td>-0.45</td>
</tr>
<tr>
<td>$q_4$</td>
<td>0.366</td>
<td>0.36</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>$q_5$</td>
<td>-1.932</td>
<td>-1.67</td>
<td>-1.88</td>
<td>-1.33</td>
</tr>
</tbody>
</table>
Using the unbalanced charges thus obtained after taking resonance into consideration, the dissociation energy $D^*$ of the bonded N—H linkage in formamide and acetamide are $5.72 \times 10^{-12}$ and $5.74 \times 10^{-13}$ erg/molecule respectively. With the values of $D^*$, the stretching frequency of the bonded N—H linkage of each amide is obtained from (3). These frequencies are given in Table III.

**Table III**

*Calculated and observed N—H stretching frequencies in cm.$^{-1}$*

<table>
<thead>
<tr>
<th>Amide</th>
<th>Free N—H stretch</th>
<th>Bonded N—H stretch</th>
<th>Calculated Without resonance</th>
<th>Calculated With resonance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formamide</td>
<td>3440</td>
<td>3210</td>
<td>3102</td>
<td>3228</td>
</tr>
<tr>
<td>Acetamide</td>
<td>3430</td>
<td>3205</td>
<td>3070</td>
<td>3234</td>
</tr>
</tbody>
</table>

The N—H stretching frequency calculated on the basis of the two resonance structures agrees fairly with the observed value in formamide, the difference being 18 cm.$^{-1}$ The length of the C=O linkage in several amides, reported by various workers$^{11, 12}$ varies from 1·22 to 1·26 Å and therefore the corresponding value in acetamide which is 1·28 Å appears to be relatively high. A consequence of the high value for the C=O linkage is a reduction in its double bond character. This explains the relatively larger deviation of 29 cm.$^{-1}$ from the observed value in the case of acetamide. In this regard it might be noted that the accuracy in the measurement of bond-length of formamide is $\pm 0.007$ Å, as given by Kurland and Wilson,$^5$ very much greater than that of acetamide which is $\pm 0.05$ Å as reported by Senti and Harker.$^6$

**VI. Summary**

The shift in the N—H stretching frequency in the infra-red spectra of amides, due to intermolecular associations, calculated on the basis that the hydrogen bonding is essentially an electrostatic interaction and that the ionic character of the bond diminishes on hydrogen bonding. The calculated and the observed values of the frequencies agree only when the two possible resonance structures in amides are taken into consideration for calculations.
VII. REFERENCES

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