Fine Structure of the NH Stretching Band of Pyrrole

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The rotational fine structure of the fundamental NH stretching band of pyrrole has been analyzed. The analysis has been based on the symmetric top approximation. The obtained rotational constants $B' = 0.3032 \text{ cm}^{-1}$, $B'' = 0.3027 \text{ cm}^{-1}$, and $C = 0.1505 \text{ cm}^{-1}$ are in good agreement with the microwave data. Also the accurate band center $v = 3530.520 \text{ cm}^{-1}$ has been obtained.

According to the microwave structural analysis of the pyrrole molecule the ratio of the two moments of inertia about the two perpendicular axes in the molecular plane is 0.986. Accordingly, the molecule is very close to an oblate symmetric top and the analysis of the rotational fine structure of the vibrational bands can be performed by applying the theory of the symmetric top molecules. The complete asymmetric top analysis of the infrared spectrum of a heavy molecule like pyrrole would be rather cumbersome and even impossible.

In this paper the fundamental NH stretching band of pyrrole has been analyzed because it fits the region of the high resolution spectrometer constructed in our laboratory. The obtained rotational constants are good approximations to the actual ones and may be compared with the microwave rotational constants. Further, the accurate band center has been obtained which is useful for the research of vibrational anharmonicities in progress at this laboratory.

Experimental

The high resolution spectrum of the NH stretching band of pyrrole was recorded by means of a large near-infrared Pfund-type grating spectrometer which has been described elsewhere. The vapor sample was in a 3-meter multiple pass absorption cell in a pressure of about 5 mm Hg. The relative humidity inside the spectrometer was about 13 per cent causing the superimposed water vapor absorptions which could be identified with the help of the paper of Plyler and Tidwell. The spectral slitwidth during the run was 0.14 cm$^{-1}$. The wavenumbers of the absorption lines were calibrated against the known emission lines of rare gases.

The pryroly used in this work was purchased from Fluka AG and was of purissim grade and used without any further purification.

Theoretical

The rotational term value which is applicable for the non-degenerate vibrational energy states is given by

$$F(J, K) = BJ(J + 1) + (C - B) K^2 - D_J B(J + 1)^2,$$

when the negligible centrifugal distortion terms dependent on $K$ have been omitted. In this case $B$ is the mean value of the actual rotational constants $A$ and $B$ of a pyrrole molecule.

The vibration of the NH stretching mode $v_0$ of pyrrole is perpendicular to the top axis. According to the selection rules of a perpendicular band, $M = \pm 1$ and $\Delta K = \pm 1$, the wavenumbers of the sub band components can be expressed in terms of $m$ which is $J - J$ in the P branch and $J + 1$ in the R branch of the band.

$$v = v_{K}^{\text{ub}} + (B' + B'') m + (B'' - B') m^2 - 4 D_J m^3.$$

The sub band origins $v_{K}^{\text{ub}}$ are given by

$$v_{K}^{\text{ub}} = v_0 + (C' - B') \pm 2(C' - B') K + [(C' - B') - (C'' - B'')] K^2$$

where $v_0$ is the wavenumber of the band center. The $+$ and $-$ signs refer to the positive $(\Delta K = 1)$ and negative $(\Delta K = -1)$ sub bands, respectively. The rotational constants of the upper state are denoted by the single prime and those of the lower state by the double prime.

Results

For the infrared fundamental bands the difference between the rotational constants of the upper and the lower state is small as a rule and thus the last term in the expression of the sub band origin should be small. The spacing of the subsequent sub bands should be $2(C' - B')$, which is about 0.3 cm$^{-1}$ according to the microwave data. On the other hand the spacing of the $J$ components should be $B' + B'' \sim 0.6$ cm$^{-1}$.

Accordingly, the sub band centers and the $J$ components of different sub bands will be superimposed with the same interval of 0.3 cm$^{-1}$. One can expect the absorptions to coincide up to rather high values of $J$ and $K$ due to the planarity and the accidental symmetry of the molecule.

On the basis of the foregoing discussion of the structure of the band a theoretical band shape was computed using the Hönl-London intensity formulae$^5$. The rotational constants reported by Bak et al.$^1$ and the temperature of 300 °K were used. The difference between the primed rotational constants was omitted. Fig. 1 illustrates the sub bands of the lowest five $K$ transitions and the resultant of sub bands up to $K=80$ when every other line has been left out. The small circles and triangles denote the portion of the negative and the positive sub bands, respectively. The cross lines indicate the portion of the $Q$ lines in the pattern.

The calculated spectrum was employed as a reference in the assignment of the spectral lines of the experimental spectrum. Also the experimental spectrum is illustrated in Fig. 1 and one can see the good agreement with the calculated one.

The $B$ constants should be calculated from single sub bands but because of the superposition of the sub bands the individual bands cannot be resolved. Each absorption line is a sum of the sub band lines of different $m$ values and as can be seen in the computed spectrum the portion of the positive sub bands in the P branch is quite small as is the portion of the negative sub bands in the R branch. The actual asymmetry and on the other hand the non-zero coefficients $B' - B''$ and $4D$ may break the coincidence of the lines when $m$ is high. Therefore it is

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not probable that a measured absorption maximum might present the wavenumber of the weak lines. An attempt was made to compute the rotational constants separately for the positive sub bands from the R branch absorptions and for the negative sub bands from the P branch absorptions. The obtained results differed too greatly, probably due to the uneven distribution of the measurable lines over the entire band (cf. Table 1). Therefore, the least square fit over the whole band was used to evaluate the rotational constants. The fits were computed for the sub bands \( K = 0, \) \( \ell = 1, \) and \( K = 1 \) simply by changing the numbering of the absorptions. In order to avoid unrealistic contribution from the unresolved sub band components, \( C' \) was taken as equal to \( C''. \) The \( C \) constant as well as the band origin \( \nu_0 \) were computed from the obtained sub band origins.

The observed and calculated wavenumbers and their differences are collected in Table 1. The calculated values have been taken from the polynomial computed for the sub band \( K = 0, \)

\[
\nu = 3530.375 + 0.60594 m - 5.10 \times 10^{-4} m^2 - 1 \times 10^{-6} m^3.
\]

The half integers of \( m \) which appear in Table 1 refer to the absorptions which belong to the sub bands with odd \( K \) values. The average difference between the measured and calculated wavenumbers is 0.014 cm\(^{-1}\). The calculated rotational constants and the wavenumber of the band center are presented in Table 2 together with the microwave data. The coefficient of the third power term in the polynomial fits of various sub bands varied so much that the \( D_j \) constant could not be evaluated reliably.

<table>
<thead>
<tr>
<th>This work</th>
<th>Nygaard et al. ²</th>
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<tbody>
<tr>
<td>( \nu_0 = 3530.520 )</td>
<td>( B'' = 0.3032 )</td>
</tr>
<tr>
<td>( A = 0.3046 )</td>
<td>( B' = 0.3027 )</td>
</tr>
<tr>
<td>( C = 0.1505 )</td>
<td>( B = 0.3003 )</td>
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<tr>
<td>Table 2. Molecular constants of pyrrole. All the values are in cm(^{-1}).</td>
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</table>

### Discussion

The rotational constants obtained agree well with the microwave data ¹, ². The differences are within the limits of the experimental errors. The difference
between \( B' \) and \( B'' \) is small, but it has been proved to be positive by a more appropriate graphical analysis. Except for the center of the \( Q \) branch, the recorded absorption band agrees well with the computed one. The slight deviation from the exact symmetric top causes the greatest discrepancies when \( K \) is small, because it is there that the strongest components of the parallel type band exist, and these transitions are allowed for in an asymmetric top molecule.\(^5\)\(^6\)

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### Radiation-Induced Conformation Changes of the Pyrimidine Ring in a Single Crystal of Dihydrothymine

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Radiation-induced radicals in a single crystal of dihydrothymine were studied with EPR. It was found that the 5-thymyl radical is the dominant radical species at room temperature. The orientation dependence of the hyperfine couplings can only be explained if one assumes that \( C(5), C(6) \) and \( C(7) \) lie in the plane defined by the rest of the nonhydrogen atoms of the ring. The highly disordered structure of the ring in the undamaged crystal is ordered if a proton bound to \( C(5) \) is removed.

Radiation damage of several dihydropyrimidines in powder and solution has been studied with electron paramagnetic resonance (EPR)\(^1\). No similar investigation in single crystals of any of these compounds has been done. In the present paper we report an EPR study of the structure of free radicals in a gamma-irradiated single crystal of dihydrothymine. The crystal and molecular structure of this compound has been reported by Furberg and Jensen\(^2\). In contrast to thymine\(^3\)\(^4\), the pyrimidine ring in the crystal of dihydrothymine is highly disordered. From the EPR study of the radiation induced radicals in a single crystal of dihydrothymine it is possible to determine whether or not the disordered structure of the ring remains unchanged after the molecule has been damaged by irradiation.

### Experimental

The crystals were grown by slow evaporation of an aqueous solution at 20 °C. No good quality crystals of moderate size could be found. Fortunately, dihydrothymine is very sensitive to irradiation and the crystal \( 1 \times 1 \times 0.2 \text{ mm}^3 \) in size was sufficient for the EPR analysis. The external configuration and the crystallographic axes of the crystal used in this study are shown in Fig. 1. The axes were identified with X-ray diffraction analysis. The crystal is orthorhombic and the dimensions of the unit cell are \( a = 7.336, b = 23.474 \) and \( c = 7.034 \text{ Å} \) (l. c.\(^2\)). There are eight molecules in the unit cell.

![Fig. 1. External configuration and the crystallographic axes of the single crystal of dihydrothymine.](image)

The crystal was irradiated in air at room temperature to a dose of about 5 Mrads by \(^{60}\)Co gamma rays, at a dose rate of 0.3 Mrads/hour. The crystal was aligned in the EPR cavity so that one of the crystallographic axes was perpendicular to the magnetic field. The spectra were recorded at room temperature with a

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\(^1\) W. Snipes and W. Bernhard, Radiat. Res. 33, 162 [1968].


