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INTERPRETATION OF THE INFRARED SPECTRA OF HYDROGEN BONDING IN 2-THIAPYRIDONE AND 2-PYRIDONE DIMERS*

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An effort was undertaken to interpret some properties of the IR spectra of 2-thiapyridone and 2-pyridone hydrogen bonded dimers. On the basis of the derived vibrational Hamiltonian of hydrogen bonds, the reasonably successful theoretical reconstitution of the experimental IR spectra of 2-thiapyridone, 2-pyridone and deuterated 2-pyridone was obtained and a fairly good agreement between the theoretical and experimental spectra was achieved. The proposed model failes in the case of interpretation of the IR spectrum of deuterated 2-pyridone. It was suggested that the shape of the N—H stretching bands is a result of strong coupling between hydrogen bond vibrations having different symmetry.

1. Introduction

The presently accepted theories of hydrogen bonding try to explain the characteristic spectral properties of hydrogen bonds i.e. the rise of intensity in the infrared spectra of the X—H stretching absorption band, the band shift towards the long-wave region, the large change of the half-width of the X—H stretching band in comparison with the analogical band of X—H group which does not take part in the hydrogen bond and the hyperfine structure of the X—H stretching band [1–4].

The last two of the above mentioned properties of the hydrogen bond spectra are the result of superfine interactions which depend upon the coupling between the high and the low frequency vibrations in hydrogen bond.

Particularly spectra of H-bonded dimers are very complicated. The structure of the IR spectra of carboxylic acid dimers was explained by Marechal and Witkowski [4]. The formalism of Witkowski and Marechal's theory was similar to that introduced earlier by Witkowski and Moffitt in their theory of vibronic coupling in dimers [6]. It assumed a model describing the coupling between the high-frequency νX—H stretching vibration and the low-frequency vibration of the hydrogen bond. The theory [4] is sufficient for interpreting the IR spectra of the carboxylic acid dimers from CH_3COOH on. The theory

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* Dedicated to Professor Kazimierz Gumiński on the occasion of his 70-th birthday.

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predicts the very characteristic shape of the νX—H absorption band. The absorption bands of the carboxylic acids H-bonds show a higher intensity in the short-wave part of the band than in the long-wave region. This regularity is observed for many other H-bonded dimers [5].

There exists a group of compounds for which this rule is not fulfilled. H-bonded 2-thiapyridone and 2-pyridone dimers can be given as an example. The IR spectra of hydrogen bonds of these dimers were measured by Bellamy and Rogasch [7]. In this paper we attempt to give an interpretation of the above mentioned property of hydrogen bonds in compounds like 2-thiapyridone and 2-pyridone.

2. *Experimental data*

The 2-thiapyridone IR spectrum was measured for the Nujol mulls and the spectrum of the 2-pyridone dimer can be obtained only when 2-pyridone is dissolved in CCl_4 [7].

In the case of 2-pyridone a great modification of the νN—H band is observed when we pass from crystals to the CCl_4 solution [7]. It is very characteristic that the spectra of 2-thiapyridone and 2-pyridone show a striking similarity in the structure and shape of their νN—H absorption bands. This fact may be explained by the very similar type of interactions in both dimers. The IR spectra of these compounds in the νN—H region are very complicated, broad and intensive. The bands are irregular, showing fine structure. The long-wave parts of the bands have a greater intensity than the remaining ones. In the spectra we can observe some groups of peaks and each group consists of a multiplet of vibrational maxima.

The 2-thiapyridone molecules in of a crystal form the crystalline lattice composed of the unit cells formed by two H-bonded dimers each [8]. In crystals of 2-pyridone we observe no dimers in the unit cells, but the molecules form H-bonded chains stretched along the crystal [9].

The three-ring structure of the dimers is isomorphic and in both dimers the hydrogen atom is connected to the nitrogen atom [7].

3. *Model*

We will discuss a simple model of a single hydrogen bond. The motions of only three atoms in the bond are considered and only the stretching motions in the hydrogen bond are taken into account. The normal coordinates for this very simplified model are:

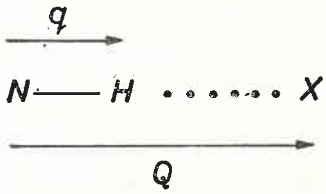

Fig. 1. The model of single hydrogen bond: q — the normal coordinate for the N—H stretching motion. Q — the normal coordinate for the N...H stretching motion. X represents the sulphur and/or the oxygen atom

the "q" coordinate describing the νN$-$H stretching vibration at a frequency of about 3400 cm^{-1} and the "Q" coordinate for the H-bond stretching vibration for low frequencies (about 100 cm^{-1}).

The reduced masses for the two vibrational modes are the m and M respectively.

The molecular structures and the sets of normal coordinates for the 2-thiapyridone and 2-pyridone dimers are presented in Fig. 2.

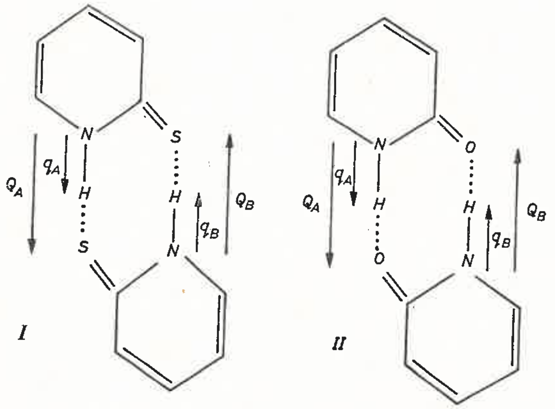

Fig. 2. Molecular structure of cyclic H-bonded dimers: I. 2-thiapyridone, II. 2-pyridone

The Hamiltonian describing the motions of the atoms in the H-bonded dimer derived by Marechal and Witkowski has the following form [4]:

$$h = \sum_{i=1}^{2} \tfrac{1}{2}(p_i^2+q_i^2)\mathbf{1}+b_{\mathrm{H}}q_1\mathbf{1}+b_{\mathrm{H}}q_2\sigma_3+C\sigma_1. \tag{1}$$

The dimensionless q_1 and q_2 coordinates are defined as:

$$q_1 = (M\omega_{\mathrm{N}\,\ldots\,X}/2\hbar)^{1/2}(Q_A+Q_B),$$
$$q_2 = (M\omega_{\mathrm{N}\,\ldots\,X}/2\hbar)^{1/2}(Q_A-Q_B), \tag{2}$$

where $\omega_{\mathrm{N}\ldots X}$ denotes the frequency of the N ... X stretching vibration.

The p_1 and p_2 are the momenta conjugated with the q_1 and q_2 coordinates.

The b_{H} and C symbols represent the distortion parameter and the resonance interaction energy between two H-bonds in the dimer. The b_{H} parameter is defined as:

$$b_{\mathrm{H}} = \hbar^{1/2}(d\omega_{\mathrm{H}}/dQ)_{Q_0}/(2M\omega^3_{\mathrm{N}\,\ldots\,X})^{1/2}. \tag{3}$$

For the theoretical reconstitution of the IR spectra of carboxylic acid dimers the C parameter was treated as independent of the low-frequency vibrations. σ_1 and σ_3 denote the Pauli spin matrices.

The form of the Hamiltonian above given does not consider the specific interactions in the H-bonded dimers of 2-thiapyridone and 2-pyridone. The characteristic property of the above mentioned dimers depends on the fact that the H-bonds join two π-electronic systems belonging to two monomers. The formation of the H-bonded dimer can be considered as a basis for obtaining some special three-ring conjugated system.

We suppose that the central ring formed by the hydrogen bonds is in some way coupled with the aromatic pyridine rings.

The magnitude of this coupling energy can be very low but the coupling energy can be comparable with the energy of the νN...X vibration.

The vibrations of the H-bonds can change the coupling energy which is sensitive to the interatomic distances in H-bonds. Besides, the halves of the dimers interact with one another through the resonance interaction term in equation (1). All these interactions lead to the complication of the IR spectra of H-bonded dimers.

The resonance interaction depends indubitably on pushing the atoms in the H-bonds out from their equilibrium positions. The coupling between the H-bonds and aromatic rings causes the resonance interaction in the case of the discussed compounds to depend stronger on the N...X distance than in the case of the carboxylic acid dimers. It implies that the C parameter is not constant during the vibrations of the H-bonds, but is a function of the low-frequency vibration coordinates:

$$C = C_0 + C_1 q_1. \tag{4}$$

The influence of the totally symmetric vibration q_1 onto the C parameter is presumably more important than the q_2 vibration because the linear term $C_2 q_2$ vanishes by symmetry.

In the case of considerable coupling of hydrogen bonds with aromatic rings, the C_0 and C_1 parameters can be comparable.

Finally the vibrational Hamiltonian of the 2-thiapyridone type dimer will have the following form:

$$h = \sum_{i=1}^{2} \tfrac{1}{2}(p_i^2 + q_i^2)\mathbf{1} + b_{\mathrm{H}} q_1 \mathbf{1} + b_{\mathrm{H}} q_2 \sigma_3 + C_0 \sigma_1 + C_1 q_1 \sigma_1 \tag{5}$$

and the functional basis of the high-frequency vibrational functions, for which the Hamiltonian has the form (5) is given by the formulas

$$\pi_A = \varphi_1(q_A, Q_A)\varphi_0(q_B, Q_B), \quad \pi_B = \varphi_0(q_A, Q_A)\varphi_1(q_B, Q_B). \tag{6}$$

The functional basis, which diagonalizes the term $(C_0 + C_1 q_1)\sigma_1$ of Hamiltonian (5), is

$$\pi_x = 2^{-1/2}(\pi_A + \pi_B), \quad \pi_u = 2^{-1/2}(\pi_A - \pi_B). \tag{7}$$

After transformation (7) of the functional basis, the Hamiltonian of the H-bonded dimer takes the equivalence formula:

$$h' = \sum_{i=1}^{2} \tfrac{1}{2}(p_i^2 + q_i^2)\mathbf{1} + b_{\mathrm{H}} q_1 \mathbf{1} + b_{\mathrm{H}} q_2 \sigma_1 + C_0 \sigma_3 + C_1 q_1 \sigma_3. \tag{8}$$

For the new functional basis (7) the physical sense of the term $C_1 q_1 \sigma_3$ is more clear. This term determines the part of the resonance interaction energy connected with the coupling of H-bonds with aromatic rings. The presence in the term $C_1 q_1 \sigma_3$ of the σ_3 Pauli matrix causes the π_x, π_u states energies to change during the totally symmetric q_1 vibration, namely the energy of one state increases and this increase can be given by some definite value, while simultaneously the energy of the other state decreases and the decrease is exactly the same as the increase in the previous case.

The π_x state corresponds to the parallel orientation of the transition moment dipoles in H-bonds of the dimer and the π_u state — to the antiparallel orientation. The coupling with the aromatic rings causes one of the dipole orientations to become more favourable than the other during the q_1 vibration. The oscillating system demonstrates a tendency to change the dipole orientation towards the more energetically favourable one.

Hamiltonian (8) is the basis for the solution of the vibrational problem and computations of the energies and intensities of transitions in the IR spectra of the dimers.

The last problem which ought to be solved is the equation below given

$$h'\begin{pmatrix}\alpha\\ \beta\end{pmatrix} = E\begin{pmatrix}\alpha\\ \beta\end{pmatrix}. \tag{9}$$

4. *Solution of the vibrational equation*

Hamiltonian (8) depends on two coordinates having different symmetry properties. It would be easy to solve equation (9) if the Hamiltonian was divided into two parts with each depending on one coordinate only. This is possible only if the obtained one-coordinate operators commute.

The commutation relation is not fulfilled because of the Pauli matrices commutation relations. The solution of equation (9) has to be performed for both types of coordinates q_1 and q_2 simultaneously.

The eigenvalue problem (9) may be simplified when the symmetry properties of the dimer molecule are taken into account. The molecule has the symmetry operation $\hat{C}_2$. It is the two-fold axis rotation operation. The operation $\hat{C}_2$ exchanges the hydrogen bonds in the dimer. Then the following commutation relation is satisfied

$$[h', \hat{C}_2\sigma_1]_- = 0. \tag{10}$$

A very similar relation exists in the case of vibronic coupling [10]. The operator (8) may be reduced by the method of Fulton and Gouterman to the two one-dimensional Hamiltonians given by the formulas

$$h^+ = \sum_{i=1}^{2} [\tfrac{1}{2}(p_i^2+q_i^2)+b_{\mathrm{H}}q_i]+\hat{C}_2C_0+\hat{C}_2C_1q_1,$$

$$h^- = \sum_{i=1}^{2} [\tfrac{1}{2}(p_i^2+q_i^2)+b_{\mathrm{H}}q_i]-\hat{C}_2C_0-C_2\hat{C}_1q_1. \tag{11}$$

Each of the operators h^+ and h^- affects the functions $\beta^+(q_1, q_2)$ and $\beta^-(q_1, q_2)$ respectively. The IR spectra of dimers are approximately the superposition of the spectra belonging to the "Plus" and "Minus" systems. With regard to the properties of the $\hat{C}_2$

operator and to the symmetry properties of the q_1 and q_2 coordinates, the operators h^+ and h^- cannot be reduced anymore. Therefore we cannot obtain the analytical resolutions. We can only get the method of solving problem (9) for an arbitrary set of parameters b_H, C_0, C_1. For this purpose we develop the functions $\beta^+(q_1, q_2)$ and $\beta^-(q_1, q_2)$ in the series of products of the harmonic oscillator wave functions:

$$\beta^{\pm}(q_1, q_2) = \sum_{k,l}^{N} d_{k,l}^{\pm,n} \varphi_k(q_1)\varphi_l(q_2), \tag{12}$$

where

$$\tfrac{1}{2}(p_i^2+q_i^2)\varphi_k(q_i) = (k+\tfrac{1}{2})\varphi_k(q_i); \qquad k+l \leqslant n$$

and n — the number of vibrational quanta of the νN ... X vibration taken into account and

$$N = \tfrac{1}{2}(n+1)(n+2). \tag{13}$$

The following secular equations must be satisfied:

$$h^{\pm}\beta^{\pm} = \varepsilon^{\pm}\beta^{\pm}. \tag{14}$$

Substitution of (12) into (14) leads to the following set of the homogeneous linear equations for the coefficients $d_{k,l}^{\pm,n}$:

$$\begin{aligned}&[k+l+C_0(-1)^l]d_{k,l}^{\pm,n}+b_H\sqrt{l/2}\,d_{k,l-1}^{\pm,n}+b_H\sqrt{(l+1)/2}\,d_{k,l+1}^{\pm,n}\\&+(b_H\pm C_1)\sqrt{k/2}\,d_{k-1,l}^{\pm,n}+(b_H\pm C_1)\sqrt{(k+1)/2}\,d_{k+1,l}^{\pm,n}=0.\end{aligned} \tag{15}$$

In order to obtain the theoretical spectra of the dimers the energies and intensities of the transitions to the “Plus” and “Minus” systems were calculated.

For $n = 10$ the corresponding energy matrices 66×66 were diagonalized on the Odra 1204 computer with the use of a program specially written for this purpose.

Because the IR spectra of the dimers were measured at room temperature, the “hot bands” were taken into account.

The parameters b_H, C_0, C_1 were chosen to get the best fit to the experimental spectra. In the case of carboxylic acid dimers the approximate b_H and C_0 parameters can be derived from the spectra [4]. In this case the choice of the set of parameters is rather arbitrary, because one spectrum is treated as a function of three parameters.

To get a better comparison between the experimental and the theoretical spectra a synthesis of the theoretical spectra from Gaussian curves was performed. We assume that the height of each curve is proportional to the intensity of a given vibrational transition and the half-width of each line is taken equal to 0.500 quanta of the νN...X vibration.

5. *Results of computations and discussion*

The results of the numerical computations are presented in Fig. 3 and Fig. 4. A good fit to the experimental spectra was obtained for the 2-thiapyridone and 2-pyridone dimers. The parameters taken into account are as follows:

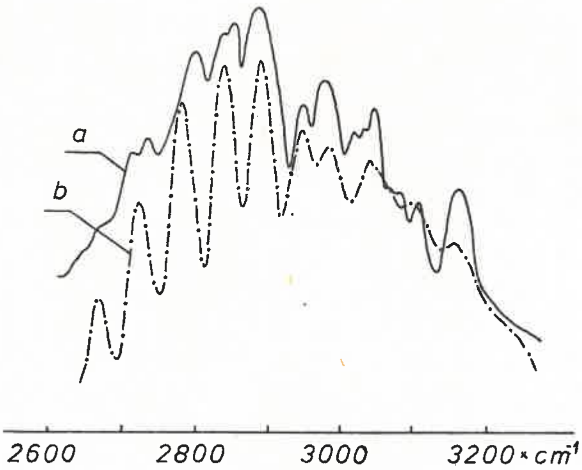

Fig. 3. *a* — Experimental IR spectrum of 2-thiapyridone dimer taken from Ref. [7]. *b* — Theoretical reconstitution of the experimental spectrum. $b_H = 1.450$, $C_0 = 1.100$, $C_1 = 0.450$, $\omega_{N...S} = 55\ \mathrm{cm}^{-1}$

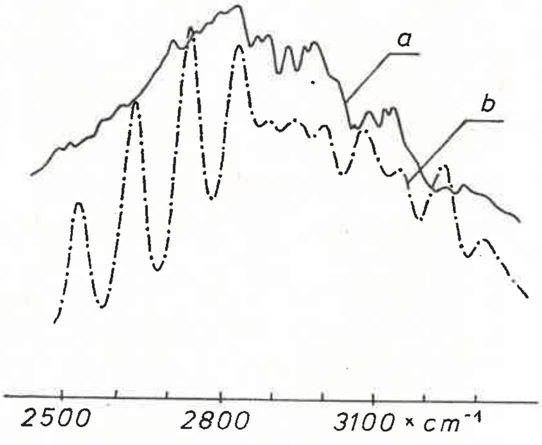

Fig. 4. *a* — Experimental IR spectrum of 2-pyridone dimer taken from Ref. [7]. *b* — Theoretical reconstitution of the experimental spectrum. $b_H = 1.600$, $C_0 = 0.900$, $C_1 = 0.500$, $\omega_{N...O} = 100\ \mathrm{cm}^{-1}$

a. For 2-thiapyridone:

$$b_H = 1.450, \quad C_0 = 1.100, \quad C_1 = 0.450, \quad \omega_{N...S} = 55\ \mathrm{cm}^{-1},$$

b. For 2-pyridone:

$$b_H = 1.600, \quad C_0 = 0.900, \quad C_1 = 0.500, \quad \omega_{N...O} = 100\ \mathrm{cm}^{-1}.$$

In spite of some inaccuracies in the theoretical reconstitution resulting from a very simple model, the theoretical reconstitution of the spectra reproduces the main properties of the dimeric νN...H bands very well. The higher intensity of the bands in the low-

-frequency region was reproduced very faithfully and the intensity distribution in the high-frequency part of the spectrum was calculated sufficiently satisfactory. The divergencies that we observe may be explained by the nontotally harmonic potential for the $\nu N...X$ vibrations. It leads to the Fermi-Resonance effect and complications in the spectra. The anharmonic potential may cause the irregularity in the progressions in the spectra and leads to the splittings at the subpeaks on the bands.

The other explanation of the splittings of the peaks in the long-wave part of the 2-thiapyridone spectrum may be the Davydow-Splitting effect. The unit cell of 2-thiapyridone crystal consists of two H-bonded dimers. Taking into account all the interactions between the H-bonds in the unit cell would only be possible if the model of four H-bonds in the unit cell was considered [11]. In our considerations we have neglected the interaction energy between the dimers in the unit cell and the interactions of the molecules in a unit cell with translationally equivalent molecules in the crystal.

The frequencies of the $N...X$ stretching vibrations taken for the reproduction of the dimeric spectra were 55 and 100 cm^{-1}. It results from the necessity of the best fit with the experimental bands. The frequencies of the low-energetic H-bonds stretching vibrations are usually somewhat higher. This difference results from the model of an isolated H-bond [4].

Some experimental facts show that the H-bonded dimers exhibit the shift in the electronic spectra and the fluorescence emission [12]. There are theories describing H-bonded dimers as the π-electronic systems [13]. Owing to these observations the assumption concerning the coupling between the H-bonds and π-electronic systems becomes more clear.

Investigations of the influence of deuteration in the H-bond onto IR spectra give the additional criterion for the adequacy of the theory of IR spectra of the H-bonded dimers.

For the carboxylic acid dimers the deuteration causes the narrowing of the $\nu O-H$ bands and some decrease in the total intensity of the band. The theory of Witkowski and Marechal [4] very well explaines the isotopic effect in the IR spectrum by the lessening of the distortion parameter b_H in the ratio $1:\sqrt{2}$.

The IR spectra of d-2-thiapyridone and d-2-pyridone are available [7] and we can compare the experimental spectra with those calculated for the parameters $b_D = b_H/\sqrt{2}$. The sets of parameters C_0 and C_1 do not change after deuteration of the H-bonds and the only change concerns the b_H parameter.

The spectrum of the d-2-pyridone dimer can be rather well reproduced for the following set of parameters:

$$b_D = 1.100, \quad C_0 = 0.900, \quad C_1 = 0.500, \quad \omega_{N...O} = 100\,cm^{-1}.$$

The IR spectrum of the hydrogen bonds of 2-thiapyridone exhibits a very strong effect of deuteration several times greater than that observed for 2-pyridone. The half-width of the $\nu N-D$ band is about ten times narrower than the half-width of the $\nu N-H$ band. A similar relation exists between the integral intensities of the bands. A very large change in the shape of the $\nu N-H$ band of 2-thiapyridone after deuteration can be observed and the deuterated compound has a very narrow band without vibrational progressions.

Such a great isotopic effect is quite unexpected and not predicted by the theories of IR spectra of hydrogen bonds.

It seems that the demonstrated properties of the H-bonds of the d and h-2-thiapyridone dimers are common for the hydrogen bonds of the N−D...S and N−H...S type. Very similar effect can be observed for hydrogen bonding in the mercaptobenzthiazole dimer [7]. It seems that the geometrical relations in the N...S bonds can give an explanation of the unusual isotopic effect. According to the crystallographical data [8] the N...S distance equals 3.26 Å. This is comparatively a very long distance since the distances between the oxygen or nitrogen atoms in a typical H-bonds are usually between 2.75 and 2.85 Å.

The N−H bond is 1.02 Å long and the position of the hydrogen atom is more asymmetric than in O−H...O or N−H...O bonds.

The properties shown by the IR spectra of the 2-thiapyridone suggest that the coupling between the oscillation motions in the N−D...S bond in the first excited νN−D state is weaker than that in the undeuterated bond. This thesis can be supported by the small intensity of the νN−D band, which is connected with the small shift of the electron charge during the νN−D oscillation.

The very small half-width of the νN−D band can be also explained by that the weaker coupling between the motions in the bond and the N and S atoms do not "sense" the excitation of the νN−D vibration. The suggestion that the N−D...S bond is weaker was proposed by the other authors as well [7].

The isotopic substitution does not change the electronic distribution in the statical model of the hydrogen bond. It seems that the amplitudes of the νN−H and νN−D vibrations can influence the magnitude of the coupling between the oscillations in the N...S by a change in the overlap between the 1*s* orbital of the hydrogen atom and the 3*p* orbital of the sulphur atom. The example of interactions in the hydrogen bonds of the 2-thiapyridone dimer is very complicated and the above presented model cannot quantitatively explain all the properties of the IR spectrum.

It seems that the case of the h and d-2-thiapyridone dimers can be described by two extreme models of coupling between the νN−H and νN−D oscillations and νN...S stretching motion: the model of the strong and weak anharmonic coupling respectively. Deuteration allows passage from one model to another.

It seems that it would be very interesting to measure the IR spectrum of d-2-thiapyridone in the first overtone band region of the νN−D vibration. The greater amplitude of the νN−D vibration in that state ought to cause a change in the shape and intensity of the νN−D overtone band. If the above presented assumptions are correct the first overtone band ought to be similar to the basic νN−H band.

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