J. Phys. Chem. A **1998,** *102,* 7603−7608

High Overtones of C−H Stretching Vibrations in Isoxazole, Thiazole, and Related Methyl and Dimethyl Derivatives

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Received: April 17, 1998; In Final Form: June 26, 1998

The high overtone spectra of liquid isoxazole and thiazole, two five-membered heterocyclic molecules with different aromaticity characters, have been investigated in the C−H stretching region by visible absorption spectroscopy. The local-mode model describes satisfactorily the C−H stretching vibrations at the fifth and sixth quanta of excitation, where the localized character is increased. Each overtone band generally displays a number of peaks corresponding to the different types of C−H oscillators. Comparison between the overtone spectra of the parent molecules and those of the methyl derivatives provided sufficient information for a conclusive assignment of the progressions. Deconvolution of the fifth overtone bands gave further evidence regarding the shape and the width of the distinct peaks. Anharmonicity values of the overtone vibrations, C−H bond lengths, and force constants were obtained from the local-mode analysis and discussed in comparison with the results obtained from the normal-mode approximation. A correlation between overtone frequencies and chemical shifts in proton magnetic resonance, generally observed in aromatic compounds, has been found only for thiazole, whose aromaticity is responsible for a significant electron current in the ring.

Introduction

The local-mode model has been satisfactorily applied to highly excited vibrational states because it offers a more appropriate description of the X−H oscillators, in terms of uncoupled anharmonic local modes, than the usual harmonic normal-mode approximation.[1−5] High overtones of the X−H vibrations (X = C, N, O) were found to have properties consistent with the chemical environment of the oscillators;[6−9] hence the study of the vibrational overtones can provide useful information on the photodissociation mechanism, radiation-less transitions of molecules, and chemical reactivity of the bonds involved in the vibrations.[10,11] This type of experimental study offers also the possibility for the investigation of the potential energy surface whose anharmonicity may be properly corrected by determining exactly the mechanical frequencies of the molecules.

Two conditions are necessary for the success of this model, a weak coupling among the oscillators and a large separation, in terms of vibrational energy, from the remaining modes of the molecule. The main coupling between the local modes derives from the kinetic energy, but it is weak if the mass ratio between X and H is very small, as in case of C−H, O−H, or N−H stretching vibrations. On the other hand, coupling due to potential energy is significant only for delocalized bonds. At low energies, as in the case of low values of the vibrational quantum number, coupling between oscillators occurs, even if weakly, and the ordinary normal-mode description, in terms of harmonic oscillators, can be considered a valid approximation. At high energies, as in case of high overtones, the local-mode model becomes the most appropriate because of the quenching of interbond coupling due to the increasing of the bond anharmonicity with the quantum number.

In this paper, we report a study of the C−H stretching overtone progressions in isoxazole and thiazole, five-membered rings containing two heteroatoms. Both molecules possess three C−H bonds which do not undergo the same chemical environments; hence three distinct overtone bands are expected in the absorption spectra. On the contrary, in furan and thiophene, two C−H stretching overtone bands are predicted in agreement with the presence in the ring of two sets of equivalent C−H oscillators.[12,13] Isoxazole and thiazole present significant differences in the spectroscopic and chemical properties. The different electron distribution in the ring is responsible for the larger aromaticity of thiazole with respect to isoxazole, whose heteroatoms strongly impair the π-electron delocalization.

Since the frequency of a high-energy overtone band is specific to an isolated chemical bond, bond lengths and force constants of the C−H oscillators were accurately evaluated by the analysis of the overtone progressions and compared with the results obtained from the normal-mode approximation.

Experimental Section

All compounds were obtained from Aldrich and Sigma (2,4-dimethylthiazole), dried on molecular sieves, and purified by repeated distillations. The spectra of the liquids at room temperature were recorded in the 3300−300 nm region on a Cary 5 spectrophotometer equipped with near-IR and visible light sources. In the overtones region of $\Delta v_{CH} = 2-4$, cells with 1- to 10-mm path lengths were used, while 4- or 5-cm path length cells (Helma) were employed for $\Delta v_{CH} = 5$ or 6. Higher signal intensities of the extremely weak fifth overtones were obtained by properly assembling two quartz cells (4- and 5-cm path length) in order to have an optical path of 9 cm.

The structures of the broad bands were analyzed through a computational deconvolution procedure in terms of Gaussian bands. Computed areas of the deconvoluted peaks differ from

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S1089-5647(98)01926-9 CCC: $15.00

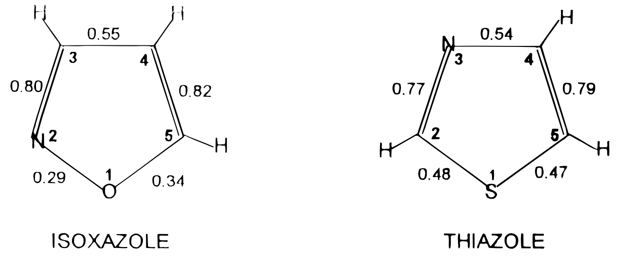

Figure 1. π bond orders of isoxazole and thiazole obtained by HMO method.

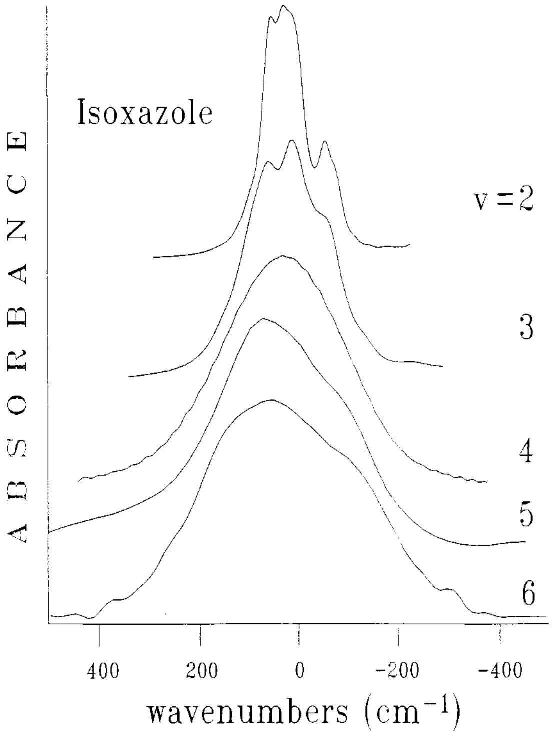

Figure 2. Band shapes of the C—H stretching overtone spectra (Δv_{CH} = 2—6) of liquid isoxazole. Room temperature.

the experimental ones by less than 1%. The bandwidth was kept constant in all experiments.

IR spectra of isoxazole and thiazole, as vapor, neat liquid, and solution, were measured with a FT-IR Bruker Model IFS-120 instrument in the C—H stretching region.

Results and Discussion

C—H Stretching Vibrations. High overtone spectra of the C—H stretching modes of isoxazole and thiazole are analyzed and discussed in comparison with those of the related methyl and dimethyl derivatives. The electronic structures of these compounds are shown in Figure 1 on the basis of the π-bond orders predicted by simple Hückel-type MO calculations.[14,15] More accurate studies indicate that isoxazole is less aromatic than oxazole, its structural isomer,[14] whereas thiazole is more aromatic than oxazole. The aromatic character of thiazole is also shown by the occurrence of a diamagnetic current induced in the ring during NMR experiments.[16]

Isoxazole. Spectra of the C—H stretching overtones (Δv = 2—6) are shown in Figure 2. The overtones at Δv = 2 or 3 exhibit the triplet structure typical of the normal modes while those at Δv = 5 or 6 progressively assume local-mode character. The fifth overtone spectrum shows a doublet structure with a separation of ~230 cm^{-1} between the two components (Figure 3). In the deconvoluted spectrum, the calculated peaks occur at 17 143 and 16 911 cm^{-1} with a 2:1 intensity ratio, indicating that two of the C—H oscillators are equivalent and overlap on the higher frequency band.

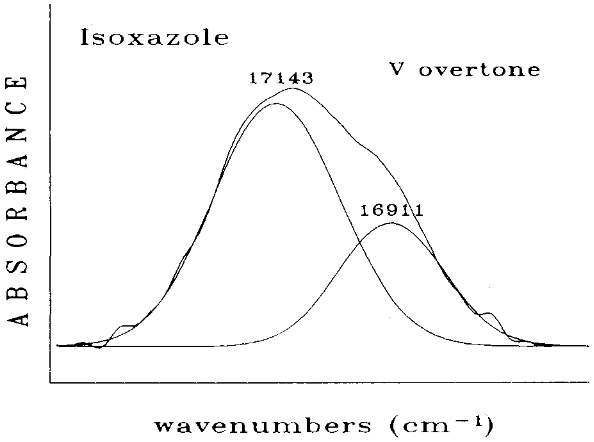

Figure 3. Resulting band profiles of the fifth C—H stretching overtone of isoxazole, calculated through a deconvolution procedure in terms of Gaussian bands.

The C—H stretching overtone progressions of the two observed frequencies have been calculated according to eq 1,

$$\nu/v = \varpi - \varpi x(v + 1) \qquad (1)$$

derived from the energy equation of the Morse diatomic oscillator, where v, ϖ, and ϖx are, respectively, the quantum number, the frequency in wavenumber, and the anharmonicity of an isolated C—H oscillator. The calculated and observed values are listed in Table 1. Only the experimental wavenumbers of the fourth and fifth overtones, provided they are of a local-mode character, have been considered in eq 1.

The fundamental harmonic frequencies (ϖ) predicted for the two local modes are 3258 ± 12 and 3220 ± 12 cm^{-1} with the same value of anharmonicity ($\varpi x = 57 \pm 2$ cm^{-1}) for both progressions. These frequencies are easily correlated with the corresponding force constants that can be calculated by considering, for each diatomic oscillator localized on the C—H bond, the reduced mass:

$$\mu = m_H m_C/(m_H + m_C) \qquad (2)$$

Our values compare very well with those obtained from ab initio calculations performed for a purely harmonic force field:[17] $K_1 = 5.413$ and $K_2 = 5.281$ mdyn/Å versus $K_1 = 5.423$ or 5.393, $K_2 = 5.356$ mdyn/Å.

We have calculated the C—H bond lengths by using the two frequencies of the fifth overtone in eq 3, developed by Gough et al.,[18,19] where r_{CH} is the length of the C—H bond in angstroms, 1.084 is the C—H bond length in benzene in angstroms, and $\Delta\nu$ is the shift in wavenumber of the overtone of isoxazole with respect to the corresponding overtone of benzene. The value of the fifth overtone in benzene[1] is 16 480 cm^{-1}.

$$r_{CH} = 1.084 - (\Delta\nu/11v)0.001 \qquad (3)$$

The resulting values, 1.077 and 1.074 Å, fit satisfactorily those obtained by microwave measurements,[20] which are 1.077, 1.074, and 1.075 Å for the C_3—H, C_4—H, and C_5—H bonds, respectively. Hence, the lower frequency progression can be attributed to the C_3—H stretching mode, while the higher frequency band undoubtedly arises from the overlap of both C_4—H and C_5—H modes. These indications are consistent with the results obtained by El-Azhary et al.[17] in the ab initio study on isoxazole,

TABLE 1: Calculated and Observed Wavenumbers of C−H Stretching Overtones in Isoxazole and Thiazole

	isoxazole		thiazole	
Δv	calcd	obsd	calcd	obsd
1	3143, 3105	3159, 3133, 3089	3123, 3086	3115, 3083, 3065
2	6172, 6095	6192, 6165, 6072	6127, 6054	6121, 6060, 6021
3	9087, 8971	9090, 9038, 8972	9013, 8903	9019, 8934, 8885
4	11887, 11732	11842	11780, 11633	11645
5	14572, 14379	14572, 14379	14429, 14245	14429, 14245
6	17143, 16911	17143, 16911	16959, 16738	16959, 16738

[a] Calculated values are obtained from the resolution of eq 1 on the basis of the experimental values of the IV and V overtones.

TABLE 2: Experimental Wavenumbers of the C−H Stretching Fundamental Vibrations of Isoxazole and Its Methyl Derivatives

compound	C_5−H	C_4−H	C_3−H
isoxazole	3159	3133	3089
5-methylisoxazole		3140	3113
3-methylisoxazole[a]	3156	3120	
3,5-dimethylisoxazole		3130	
3,4-dimethylisoxazole[a]	3156		
4,5-dimethylisoxazole[a]			3080

[a] Values taken from ref 21.

where several methods of calculation are employed to determine the equilibrium geometry and the length of the C−H bonds. Regardless of the choice of the applied method, the C_3−H bond length is always longer than those of the C_4−H and C_5−H bonds, whose lengths are quite comparable. In particular, the C−H bond lengths calculated by the MP2/6-31G** method match the values obtained from both microwave and overtone experiments. According to the normal-mode analysis,[17] the C_3−H stretching mode is uncoupled and corresponds to the lower frequency band. The other two fundamentals observed at 3159 and 3133 cm^{-1} arise from the coupling between C_4−H and C_5−H stretching vibrations. These data contrast with those of ref 21 where, on the basis of force constant calculations, the three C−H stretching modes are described in terms of uncoupled vibrations.

Overtone spectra of mono- and dimethylisoxazoles give a further contribution to the assignment of the C−H stretching modes. From the inspection of Table 2, where the normal-mode frequencies of isoxazole and methylisoxazoles are compared, it is possible to localize the C_5−H and C_3−H stretching modes. However, conclusive results are obtained by the analysis of the overtone spectra of the methyl derivatives that exhibit simpler patterns than that of isoxazole because of the reduced number of C−H bonds. For example, in the case of 5-methylisoxazole, whose spectra shown in Figure 4 are limited to the fourth instead of the too-weak fifth overtone, the two well-defined absorption peaks at 14 574 and 14 373 cm^{-1} are clearly attributable to the C_4−H and C_3−H stretching vibrations, respectively. As shown in Figure 5, both peaks have practically the same intensity and correspond to the doublet present in isoxazole, which appears with a 2:1 band intensity ratio due to the overlapping of the C_5−H and C_4−H stretching modes. In the same figure, we also report the fourth overtone spectrum of 3,5-dimethylisoxazole showing a single band at ~14 520 cm^{-1} clearly related to the C−H oscillator at position 4.

According to these observations, it is possible to draw some conclusions. The lower frequency band corresponds to the C_3−H stretching, whereas the C_4−H and C_5−H stretching vibrations are practically equivalent and give rise to the higher frequency band. In 3,5-dimethylisoxazole, the band corresponding to the C_4−H stretching vibration undergoes a downshift of ~50 cm^{-1} with respect to the spectrum of isoxazole. An analogous downshift (35 cm^{-1}) was found for the fifth overtone of 3-methylthiophene.[12] In our experience, the inductive effect of the methyl groups adjacent to the C_4−H bond increases the charge density on the carbon atom and lengthens the bond of this oscillator. It causes the decrease of the corresponding force constant and the shift of the overtone to lower energy.

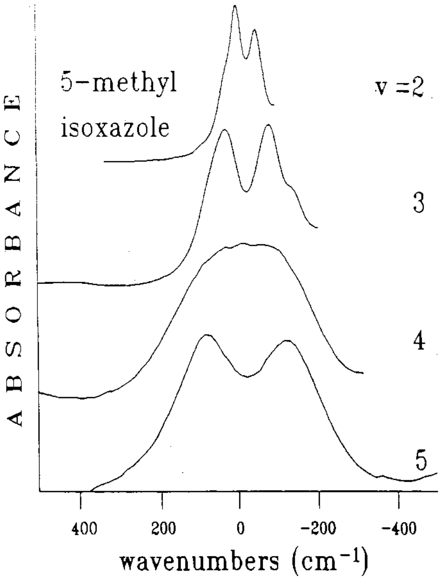

Figure 4. Band shapes of the C−H stretching overtone spectra (Δv_{CH} = 2−5) of liquid 5-methylisoxazole. Room temperature.

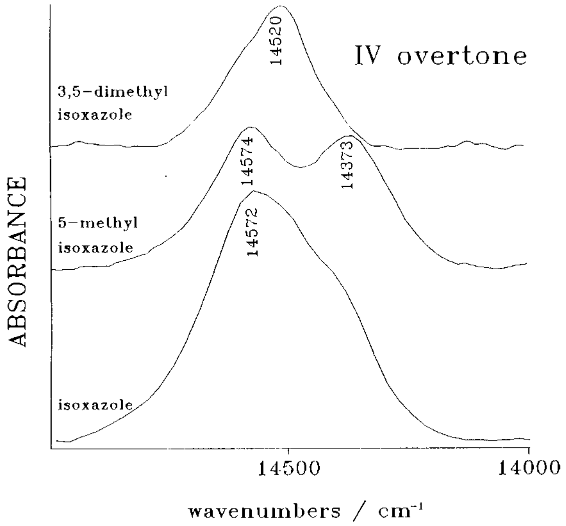

Figure 5. The fourth overtone spectra of the C−H stretching vibrations of liquid isoxazole, 5-methylisoxazole, and 3,5-dimethylisoxazole. Room temperature.

Thiazole. The overtone spectra of thiazole are shown in Figure 6 for Δv = 2−6, but the local-mode model interprets only the overtone progressions with Δv = 5 or 6, as previously

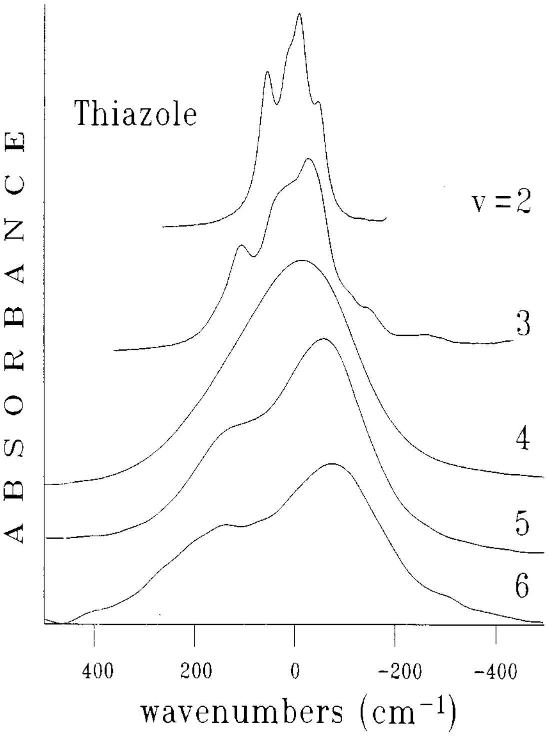

Figure 6. Band shapes of the C−H stretching overtone spectra ($\Delta v_{CH} = 2-6$) of liquid thiazole. Room temperature.

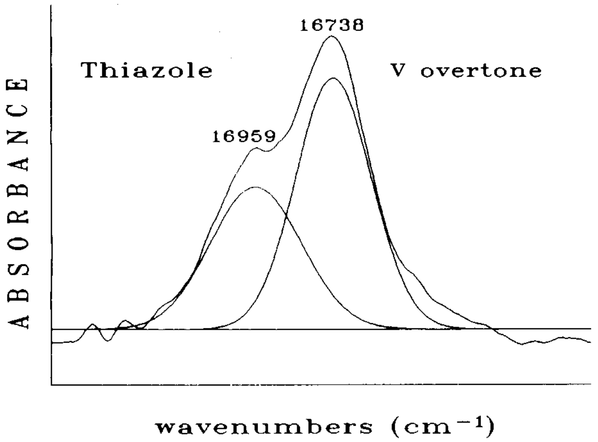

Figure 7. Resulting band profiles of the fifth C−H stretching overtones of thiazole, calculated through a deconvolution procedure in terms of Gaussian bands.

observed in isoxazole. In the fifth overtone spectrum, only two absorption bands occur at 16 959 and 16 738 cm^{-1}, despite of the presence of three different C−H bonds. The 1:2 intensity ratio between these peaks indicates that two C−H oscillators are equivalent and overlap in the lower frequency band. In isoxazole, we found the opposite situation with a 2:1 intensity ratio of the doublet at 17 143 and 16 911 cm^{-1}. In thiazole, the peak separation, calculated from the deconvolution of the fifth overtone, is ~220 cm^{-1} (Figure 7), analogous with the value of 230 cm^{-1} found for isoxazole.

The overtone progressions of the C−H stretching bands, calculated from the Morse equation, are listed in Table 1. The harmonic fundamental frequencies (ϖ) of the two local modes have been calculated to be 3242 ± 12 and 3205 ± 12 cm^{-1} with a value of anharmonicity of 59 ± 2 cm^{-1} (59 cm^{-1} in thiophene[12]), equal for both progressions. As shown in Table 1, the fundamental frequencies as well as the overtone peaks of thiazole are downshifted with respect to those of isoxazole.

TABLE 3: Experimental Wavenumbers of the C−H Stretching Fundamental Vibrations of Thiazole and Its Methyl Derivatives

compound	C_5−H	C_4−H	C_2−H
thiazole	3119	3084	~3065[b]
5-methylthiazole[a]		3073	
4-methylthiazole	3105		3080
2-methylthiazole[a]	3115	3086	
2,5-dimethylthiazole[a]		3086	
2,4-dimethylthiazole	3109		
4,5-dimethylthiazole			3060

[a] Values taken from ref 22. [b] From crystal ref 23.

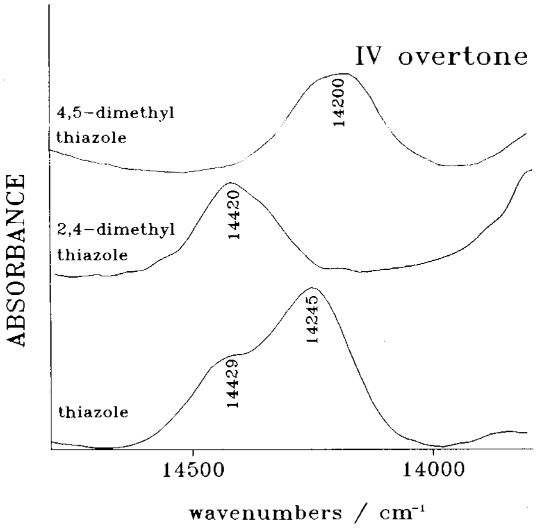

Figure 8. The fourth overtone spectra of the C−H stretching vibrations of liquid thiazole and 2,4- and 4,5-dimethylthiazole. Room temperature.

Evidence of the downshift is also given by the smaller values of the force constants obtained from the local-mode analysis, K_1 = 5.343 and K_2 = 5.217 mdyn/Å. These observations indicate that the C−H oscillators of the two molecules undergo different electronic environments, related with π-electron delocalization.

Microwave[24] and overtone spectra of thiazole do not provide sufficient information for a certain identification of the three C−H oscillators. A length of 1.077 Å was determined by microwave experiments for both the C_2−H and C_5−H bonds, and a value of 1.080 Å was attributed to the C_4−H bond length. According to the local-mode model, by using the frequencies of the fifth overtone in eq 3, we have calculated values of 1.077 and 1.080 Å which, contrary to the microwave data, indicate the presence in the ring of only one shorter C−H bond. These results are confirmed by ab initio calculations based on MP2/6-31G** [25] and DFT/6-31G** [26] methods, which locate both C_2−H and C_4−H stretching modes at ~3090 cm^{-1} and the C_5−H stretching vibration at ~3130 cm^{-1}, in correspondence with the higher frequency band.

The disagreement observed between the bond lengths determined by different experimental techniques was recently discussed in a work on pyridine and mainly attributed to the uncertainties of the microwave values.[27] In our case a determinant contribution is provided by the spectral analysis of the methyl derivatives (Table 3) and in particular by the overtone spectra of 2,4- and 4,5-dimethylthiazole, which are characterized by the presence of a single band and therefore easy to interpret. In Figure 8 the liquid spectra of dimethyl derivatives, overlaid on the thiazole spectrum, are shown in the $\Delta v_{CH} = 5$ region. This comparison indicates that the overtone at 14 429 cm^{-1} in

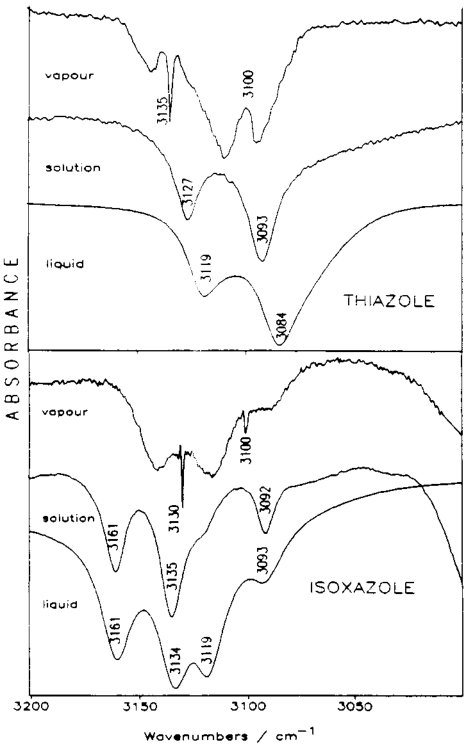

Figure 9. Infrared spectra in the C−H stretching region of isoxazole and thiazole in vapor (10 cm path length), CCl_4 solution (1-mm-thick cell), and liquid film. Room temperature.

thiazole, corresponding to the band of the 2,4-dimethyl derivative at ∼14 420 cm^{-1}, can undoubtedly be ascribed to the C_5−H oscillator. The spectrum of the 4,5-dimethylthiazole displays only a C−H stretching overtone at ∼14 200 cm^{-1}, which must be attributed to the C_2−H bond. Hence, it is reasonable to conclude that the lower frequency overtone of thiazole at 14 245 cm^{-1} is associated with the C−H oscillators at positions 2 and 4 in the ring. The substituent effect, previously observed for the C_4−H stretching band of isoxazole, is still evident in the 4,5-dimethylthiazole, where the C_2−H stretching overtone undergoes a downshift of ∼45 cm^{-1}.

These results confirm the importance of the local-mode model in determining the bond lengths of the C−H oscillators. In isoxazole, the calculated values are in good agreement with those obtained from the microwave spectra, while in thiazole, a longer bond length is ascribed to the C_2−H bond (1.080 instead of 1.077 Å) by the local-mode model. This discrepancy could be due to the fact that the microwave spectra were obtained in the vapor phase, where the molecular associations present in the liquid phase are missing. Hence, we have reinvestigated the infrared spectra of the vapor, solution, and liquid phases of both molecules in the C−H stretching region (Figure 9) to evaluate the contribution of intermolecular forces in the various states of aggregation. No important frequency shift occurs in the isoxazole spectra going from vapor to solution to liquid, whereas this effect is quite visible in thiazole, whose bands undergo a progressive downshift. This is indicative of the presence in the liquid state of intermolecular associations involving the C−H groups.[28] In particular, it is likely to suppose the existence of intermolecular interactions between the negatively charged part of the molecule, mainly located on the nitrogen atom, and the C_2−H group of another molecule because of the great acidity of the hydrogen atom at position 2.[29] This fact can justify the lengthening of the C_2−H bond observed in the liquid phase with respect to the microwave data. In the vapor phase, no interaction exists between molecules; hence the bond lengths determined by the microwave spectroscopy are those of the isolated molecule.

Relation between C−H Stretching Overtones and Proton Chemical Shifts. In a paper on the overtone spectra of six-membered aromatic heterocycles,[30] the C−H stretching frequencies were correlated with the chemical shifts in the proton magnetic resonance. As previously observed, there is a close correlation between bond strength and bond length, which can be easily obtained from the local-mode analysis. The bond strength is related to the electron densities around the nuclei involved in the bond. On the other hand, the chemical shifts depend on the relative electron densities in close proximity to the hydrogen atoms. Hence, we have compared the NMR data reported in the literature for isoxazole[31] and thiazole[32] with those obtained from the overtone study. As shown below, a good agreement occurs between the bond lengths (d) and the proton chemical shifts (δ) in thiazole, whereas this correlation fails for isoxazole:

$$\text{isoxazole} \quad d(C_3{-}H) > d(C_4{-}H), d(C_5{-}H)$$
$$\delta(H_5) > \delta(H_3) > \delta(H_4)$$

$$\text{thiazole} \quad d(C_2{-}H), d(C_4{-}H) > d(C_5{-}H)$$
$$\delta(H_2) > \delta(H_4) > \delta(H_5)$$

Because of the considerable π-electron delocalization, thiazole can be regarded as an aromatic molecule. The effect of the ring current caused by the π electrons on the proton chemical shifts is expected to be similar to that observed in the six-membered aromatic molecules. This fact can account for the correlation between chemical shifts and net π charges observed in thiazole as well as in thiophene.[33] In isoxazole, the heteroatoms impair the delocalization of the π electrons; thus the anisotropy of the localized double bonds affects the proton magnetic resonance differently. Hence, as previously reported, a relationship between overtone frequencies and proton chemical shifts occurs only in cyclic compounds where the electron density is quite uniformly distributed in the ring. This type of correlation has, however, a limited validity since it compares observables obtained from spectroscopic techniques (NMR and IR) which study different molecular properties.

Conclusions

According to the local-mode model, the overtone spectra of isoxazole and thiazole are successfully analyzed and the C−H stretching progressions are interpreted with the aid of the corresponding methyl derivatives. This procedure allows the determination of C−H bond lengths and the evaluation of suitable values of force constants as well as the anharmonicity of the overtone bands. The correlation between the data obtained from the C−H stretching overtones and the chemical shifts in the proton magnetic resonance has been proven, but it holds only for aromatic or pseudo aromatic molecules.

Comparison with the overtone spectra of oxazole and isothiazole would allow a more complete analysis of the C−H stretching progressions by the evaluation of the effect of the relative positions of the two heteroatoms in the ring. The impossibility of obtaining a large amount of sample, as necessary in the optical measurements, prevented us from extending this investigation to the overall compounds. Thermal lensing and photoacoustic spectroscopies represent alternative techniques, even if more complex than the present procedure, for the investigation of the high overtones by employing a small amount of sample.

Acknowledgment. Financial support from the Italian Consiglio Nazionale delle Ricerche and Ministero della Pubblica Istruzione is gratefully acknowledged.

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