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### Vibrational Spectra of Thiazole-2-Carboxylic Acid and Thiazole-2-Carboxylate Ion

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VIBRATIONAL SPECTRA OF THIAZOLE-2-CARBOXYLIC ACID  
AND THIAZOLE-2-CARBOXYLATE ION

key words: infrared, Raman, vibrational spectra, thiazole-2-carboxylic acid.

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**ABSTRACT**

The i.r. spectra of thiazole-2-carboxylic acid and thiazole-2-carboxylate ion as CsI pellets and Nujol mull as well as Raman spectrum of an aqueous solution of the salt have been investigated. Most vibrations have been assigned on the basis of group frequencies and by correlation between the spectra of both molecules. The -COOH characteristic vibrations have been assigned as vibrations of the intermolecularly associated species.

**INTRODUCTION**

The vibrational spectra of the carboxylic acids have been studied by different authors, generally presenting several difficulties being among them not only those derived from the intermolecular association in

the solid state but also those of their low solubility in water making the record of Raman spectra of solution and the determination of the depolarization ratios nearly impossible<sup>1-3</sup>. However, the salts of these acids can be prepared fairly easily and they are soluble in water in proportions high enough to record the Raman spectra of aqueous solutions, thus usually turning out to be very useful for correlations with the spectra of the respective acids. Few thiazole-2-carboxylate derivatives are described in the literature<sup>4,5</sup>, usually appearing as ethyl esters since a vibrational assignment for neither thiazole-2-carboxylic acid nor its thiazole-2-carboxylate ion has been discussed yet.

In this work, we have investigated the i.r. spectra of the acid in the solid state and in dimethyl-sulfoxide (DMSO) solution and the i.r. spectrum in solid state and Raman spectrum of aqueous solution of the salt, taking into account the assignment proposed on the thiazole molecule<sup>6</sup>, the possibility that intermolecular associations may occur by hydrogen bonding<sup>7</sup>, as well as the possible existence of rotational isomers for the thiazole-2-carboxylic acid molecules<sup>5</sup>.

#### EXPERIMENTAL AND RESULTS

The thiazole-2-carboxylic acid was obtained from Dr. Henning Lund and synthesized by Palle E. Iversen<sup>8</sup>, University of Aarhus, Denmark, and used without further purification. The salt was obtained by dissolving the acid in a stoichiometric amount of an aqueous solution of KOH and then the solvent was evaporated. Infrared spectra of KBr and CsI pellets and Nujol mull were recorded on a Perkin Elmer 783 spectrophotometer. As thiazole-2-carboxylic acid does not dissolve in ordinary solvents, the i.r. spectrum on a diluted solution of

dimethylsulfoxide was carried out. In this way, the assignment of a few bands in solution could be obtained. The standards used for wavenumber determinations were polystyrene+camphor+cyclohexanone as described in ref.<sup>9</sup>. The Raman spectrum was recorded on a Jobin Yvon U-1000 spectrometer fitted with a Spectra Physics Ar<sup>+</sup> laser using the Ar<sup>+</sup> 5145 Å exciting line.

## DISCUSSION

### Symmetry of vibrations

The molecular structure of the thiazole-2-carboxylic acid has so far not been determined experimentally. However, taking into account the planar structure of thiazole<sup>10</sup>, a planar structure for both molecules has been assumed with a relevant C<sub>8</sub> point group of symmetry. In the acid such planar structure leaves the C=O group in the proximity of either the nitrogen or the sulphur atom of the heterocyclic system, and this leads us to think that the stretching carbonyl mode must give rise to a doublet of absorption with an appreciable separation between the components. Moreover, it has been proved that the -COOH group is linked intermolecularly by hydrogen bonding to the basic thiazolinic nitrogen<sup>7</sup>, just as it occurs in other compounds e.g. imidazole, triazole and hydantoins<sup>11</sup>. These compounds have an acid center an a basic one in the same molecule; in this way, C<sub>8</sub> symmetry is maintained and considering the molecule individually there are for the acid 27 normal vibrations, 19 belonging to symmetry species A' and 8 belonging to symmetry species A". In the case of the ion, there are 24 normal vibrations, 17 A' + 7 A".

### Assignment

In the following paragraphs, we will discuss the proposed assignment for the observed i.r. and Raman

TABLE 1

Summary of Frequencies and Assignments in Infrared Spectra of Thiazole-2-carboxylic acid.

Solid		Solution		Assignment
I	v	I	v	
s <sup>a</sup>	239.6			$\gamma$ (CX);A"
w	263.6			2xt(OCO);A'
w	390.2			$\delta$ (CX);A'
s	461.4	w	460.4	r(OCO);A'
m	479.4			$\Gamma_2$ ;A"
s	610.3	m	611.9	$\Gamma_1$ ;A"
w	655.4	sh	652.1	$\delta$ (OCO);A'
m	665.8	m	670.5	$W_7$ ;A'
w	736.4			$W_2$ - $\delta$ (OCO);A'
s	755.8	m	749.1	$\gamma_3$ (CH);A"
s	765.5			$W_6$ ;A'
vs	776.5	s	774.1	$\gamma$ (OCO);A"
s	787.2	sh	788.6	$\gamma_2$ (CH);A"
vw	890.2	w	865.5	$W_5$ ;A'
m	908.5	m	899.9	$W_4$ ;A'
mb	991.8			$\gamma$ (OH);A"
vs	1064.3			$\delta_3$ (CH);A'
w	1089.4			$\Gamma_1+\Gamma_2$ ;A'
s	1124.8			$\delta_2$ (CH);A'
vs	1152.7	w	1152.6	$\nu$ (CX);A'
sb	1273.1			$W_3$ ;A'
sh	1320.4			$W_6+\Gamma_1$ ;A"
sh	1385.1			$\gamma$ (OCO)+ $\Gamma_1$ ;A' $W_4+\Gamma_2$ ;A"

TABLE 1 (cont.)

Solid		Solution		Assignment
I	v	I	v	
s	1398.4			$\nu_2$ ; A'
s	1436.7			$\delta$ (OH); A'
m	1491.3	m	1491.9	$\nu_1$ ; A'
sh	1550.3			$2\nu\gamma(OCO)$ ; A'
sh	1623.1	w	1657.4	$\nu_6 + \nu_2$ (CH); A'' $\nu(CX) + \nu_2$ ; A''
m	1702.7	sh	1692.3	$\nu_{sym}$ (C=O); A'
s	1735.6	s	1712.9	$\nu_{anti}$ (C=O); A'
sb	1880.2			$\nu$ (OH); A'
sh	2181.7			$\nu_4 + \nu(C-O)$ ; A' $\nu_2 + \nu_2$ (CH); A''
sb	2413			$\nu(C-O) + \nu(CX)$ ; A' $\delta$ (OH) + $\gamma$ (OH); A''
sb	2495			$\nu$ (OH); A'
sb	2572			$\nu(CX) + \delta$ (OH); A'
w	2606			$\nu_4 + \nu(C=O)$ ; A'
m	2665			$\nu_2 + \nu(C-O)$ ; A'
s	2727			$\nu$ (OH); A'
m	2833			$\nu_2 + \delta$ (OH); A'
s	3109.9			$\nu_2$ (CH); A'
s	3126.5			$\nu_1$ (CH); A'

a

Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

TABLE 2

Summary of frequencies and assignments in infrared and Raman spectra of thiazole-2-carboxylate ion.

i.r. solid		Raman solution <sup>a</sup>			Assignment
I	v	I	v	p	
w <sup>b</sup>	247.0				$\gamma$ (CX); A"
vw	286.0				2xt(OCO); A'
m	390.1				$\delta$ (CX); A'
w	464.2				r(OCO); A'
w	490.9				$r_2$ ; A"
s	602.1				$r_1$ ; A"
w	655.8				$\delta$ (OCO); A'
		w	660	p	$w_7$ ; A'
s	721.3	vw	724		$\gamma_3$ (CH); A"
m	766.2	vw	772		$w_6$ ; A'
s	792.2				$\gamma$ (OCO); A"
s	797.2				$\gamma_2$ (CH); A"
w	881.4	w	884	p	$w_5$ ; A'
w	890.2				$w_4$ ; A'
vw	1036.4				$\delta$ (OCO)+ $\delta$ (CX); A'
					$\gamma$ (OCO)+ $\gamma$ (CX); A'
m	1050.5	vw	1060		$\delta_3$ (CH); A'
vw	1065.6				$r$ (OCO)+ $r_1$ ; A"
s	1096.7				$\delta_2$ (CH); A'

TABLE 2 (cont.)

i.r. solid		Raman solution			Assignment
I	v	I	v	p	
sh	1115.6				$\tau(\text{OCO}) + \delta(\text{OCO}) ; \text{A}'$
w	1159.8	w	1163	p	$\nu(\text{CX}) ; \text{A}'$
vw	1251.8				$\tau(\text{OCO}) + \gamma(\text{OCO}) ; \text{A}''$
vw	1282.9				$\tau_2 + \gamma(\text{OCO}) ; \text{A}'$
m	1314.6				$w_3 ; \text{A}'$
vs	1362.1				$w_2 ; \text{A}'$
sh	1396.5				$\tau_1 + \gamma_2(\text{CH}) ; \text{A}''$
s	1416.3	m	1412	p	$\nu_s(\text{OCO}) ; \text{A}'$
w	1448.1				$\delta(\text{OCO}) + \gamma(\text{OCO}) ; \text{A}''$
vw	1478.1				$w_5 + \tau_1 ; \text{A}''$
s	1495.1	m	1494	p	$w_1 ; \text{A}'$
w	1554.2				$w_6 + \gamma(\text{OCO}) ; \text{A}''$
w	1582.9				$2\gamma(\text{OCO}) ; \text{A}'$
sb	1645.5	w	1642		$\nu_{as}(\text{OCO}) ; \text{A}'$
w	1775.5				$w_3 + \tau(\text{OCO}) ; \text{A}'$
w	3082.8				$\nu_2(\text{CH}) ; \text{A}'$

<sup>a</sup> Due to the high fluorescence, only a few fundamentals have been identified and only for some of these bands was possible to evaluate the depolarization ratio.

<sup>b</sup> Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

bands for each compound which are shown in Tables 1 and 2. Vibrations have been divided for their discussion into: ring vibrations, CH vibrations and vibrations of the substituent.

#### Thiazole-2-carboxylic acid

Ring vibrations. The vibrations in the spectra of thiazole and derivatives were studied in detail prior to this work.<sup>6</sup>

In the thiazole-2-carboxylic acid the bands corresponding to  $W_1;A'$ ,  $W_7;A'$  and  $\Gamma_1;A''$  were recorded and assigned in both solid and solution i.r. spectra while the bands assigned to  $W_2;A'$ ,  $W_3;A'$ ,  $W_6;A'$  and  $\Gamma_2;A''$  modes could not be seen in DMSO solution. The frequencies of these vibrations apparently do not change with respect to the values for thiazole. The breathing mode  $W_5;A'$  as well as  $W_4;A'$  was recorded in both solid and solution i.r. spectra but at higher frequencies in the solid state than in the thiazole, although the same band structure is maintained.

CH vibrations. The two stretching modes for the -CH bonds in 4 and 5 positions,  $\nu_1(CH)$  and  $\nu_2(CH)$ , were recorded as a very strong bands in the i.r. spectrum in the solid phase at  $3126.5\text{ cm}^{-1}$  and  $3109.9\text{ cm}^{-1}$  appearing a few wavenumbers higher than in the spectrum of thiazole. The two bending vibrations,  $\delta(CH)$ , were also recorded in the solid i.r. spectrum and assigned to the strong bands at  $1124.8\text{ cm}^{-1}$  and  $1064.3\text{ cm}^{-1}$  and both  $\gamma(CH)$  corresponding to the out-of-plane deformations, were observed in the solid and solution i.r. spectra at  $787.2\text{ cm}^{-1}$  and  $755.8\text{ cm}^{-1}$  corresponding with those which appeared at  $799.4\text{ cm}^{-1}$  and  $722.0\text{ cm}^{-1}$  for the thiazole vapour.

Vibrations of the substituent. Assuming the  $C_s$  point group as relevant for any characteristic vibration, the vibration  $\nu(OH)$  appears as a consequence of the strong association between the acid group and the basic thiazolinic nitrogen<sup>7</sup> in form of three characteristic bands usually called "A", "B" and "C", located at  $2750\text{ cm}^{-1}$ ,  $2450\text{ cm}^{-1}$  and  $1880\text{ cm}^{-1}$ , respectively. The vibration  $\nu(C=O)$  appears in the form of a doublet of absorption with a separation of  $30\text{ cm}^{-1}$ , one band at  $1735.6\text{ cm}^{-1}$  in the solid i.r. spectrum due to the anti-s-trans isomer and the other at  $1702.7\text{ cm}^{-1}$  in the solid and at  $1692.3\text{ cm}^{-1}$  in the solution spectrum due to the sym-s-trans<sup>7</sup>. The remaining assignment in Table 1 are based mainly on a correlation with the spectra of other carboxylic acids. Concerning the vibration  $\tau(OCO);A''$ , which usually appears at a frequency lower than  $200\text{ cm}^{-1}$ , a band at  $263\text{ cm}^{-1}$  as  $2 \times \tau(OCO)$  was tentatively assigned, thus the vibration  $\tau(OCO)$  would be lied around  $135\text{ cm}^{-1}$ , a value close to the same found for benzoic acid<sup>2</sup>.

Overtone, combination and difference bands. Some weak bands recorded in the solid i.r. spectrum of thiazole-2-carboxylic acid can be assigned as overtone, combination or difference bands and their assignment are included in Table 1. Thus, the bands recorded in the  $3000-2400\text{ cm}^{-1}$  region were assigned to combinations of characteristic vibrations of the -COOH group, as can be seen in Table 1.

#### Thiazole-2-carboxylate ion

Ring vibrations. All  $A'$  and  $A''$  vibrations were assigned by correlation with the spectra of thiazole-2-carboxylic acid, being recorded at frequencies near those for the acid, except  $W_2$ , which is found at a slightly lower frequency (Table 2).

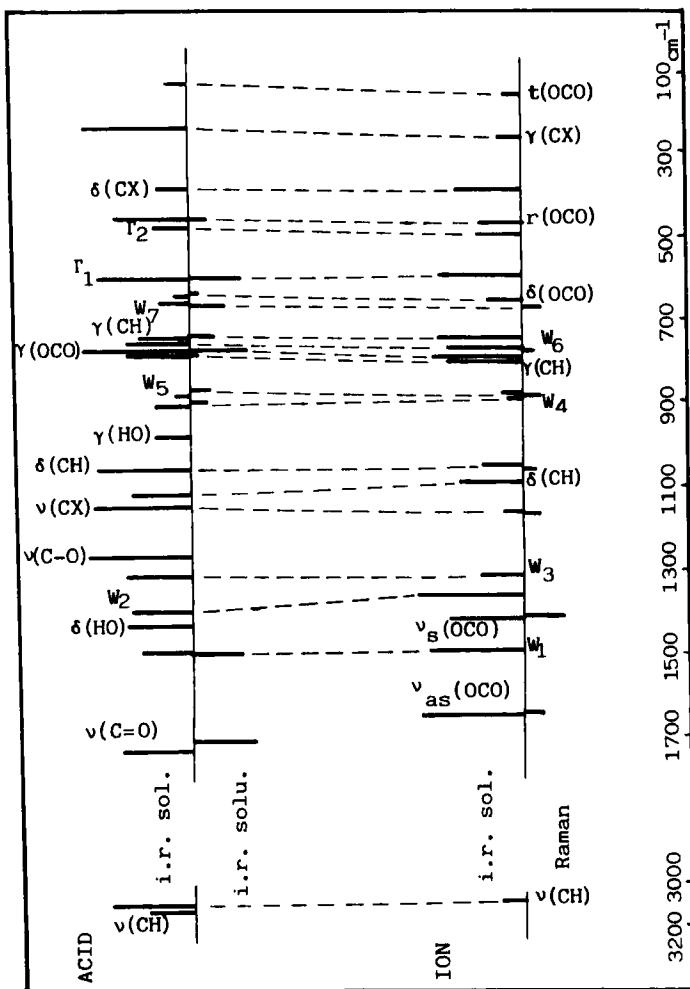


FIG. 1. Correlations of the i.r. and Raman frequencies of thiazole-2-carboxylic acid and thiazole-2-carboxylate ion.

CH vibrations. Only one CH stretching vibration,  $\nu(\text{CH})$ , appears in the solid i.r. thiazole-2-carboxylate ion spectrum, coinciding with the one which appears at  $3080 \text{ cm}^{-1}$  for thiazole. The in-plane deformation vibrations  $\delta(\text{CH})$  appear at  $1096.7 \text{ cm}^{-1}$  and  $1050.5 \text{ cm}^{-1}$ , at frequencies slightly lower than for the acid, but the second one is only recorded in the Raman spectrum. Finally, the out-of-plane deformation vibrations  $\gamma(\text{CH})$  were assigned by correlation with thiazole, appearing slightly shifted with respect to the acid.

Vibrations of the substituent. For the ion, as we expected, the disappearance of the bands corresponding to the carboxylic acid group and the appearance of the corresponding bands  $\nu_{\text{as}}(\text{OCO})$  and  $\nu_{\text{s}}(\text{OCO})$  are observed, the latter one in both the i.r. and Raman spectra (Table 2). The remaining vibrations in the -COO group appear at frequencies similar to the acid, but  $\gamma(\text{OCO})$  is slightly shifted to higher frequencies for the ion with respect to the acid (Fig. 1). Once again, the vibration  $\text{t}(\text{OCO})$  is expected to be under  $200 \text{ cm}^{-1}$ , and the band at  $286 \text{ cm}^{-1}$  is tentatively assigned as  $2 \times \text{t}(\text{OCO})$ ; Therefore a frequency close to  $145 \text{ cm}^{-1}$  is expected for the fundamental as a consequence of the anharmonicity of the vibrations.

Combination and overtone bands. Many combination and overtone bands were assigned and can be seen in Table 2. The only reasonable assignment that we found for the weak band recorded on the i.r. spectrum at  $1448.1 \text{ cm}^{-1}$  was  $\delta(\text{OCO}) + \gamma(\text{OCO}); \text{A}''$ , and was mentioned previously, for the band at  $286 \text{ cm}^{-1}$ , it can only explained as the overtone  $2 \times \text{t}(\text{OCO}); \text{A}'$ .

#### FINAL REMARKS

Figure 1 gives the correlations of the i.r. and Raman frequencies of the ring and substituent fundamen-

tals involving the  $-COOH$  and  $-COO$  characteristic vibrations. They are very stables with the exception of  $\omega_2$  and  $\gamma(OCO)$ , which increase in frequency in the ion with respect to the acid. The same behaviour observed by Claydon and Sheppard<sup>12</sup> for the vibration  $\nu(OH)$  in compounds having one acid center and another basic one was seen by us, which is sufficient evidence to confirm the hypothesis that the vibration of the  $-COOH$  group must be considered as a vibration of the intermolecularly associated species  $-COOH---N_c$  with possibly the rotational isomers anti-s-trans and sym-s-trans.

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