A VIBRATIONAL STUDY OF TAUTOMERISM AND ASSOCIATIONS OF 2-MERCAPTOIMIDAZOLE AND 2-MERCAPTOTHIAZOLE

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Infrared and Raman spectra of 2-mercaptoimidazole and 2-mercaptothiazole in solid state as well as i.r. spectra of 2-mercaptothiazole in $HCCl_3$ and CS_2 0·05M solutions have been investigated. A general assignment of all the observed bands is proposed for both fundamental vibrations and for overtone and combination bands. For 2-mercaptothiazole, the thiocarbonyl-form, intermolecularly hydrogen-bonded dimers in solid state, and unassociated molecules in dilute solutions of inert solvents have been established. Finally, based on this data, thermodynamic functions have been computed.

The α- and γ-mercapto derivatives of N-heteroaromatic compounds are capable of tautomerism. In order to differentiate between the mercapto-form and thiocarbonyl-form by means of an i.r. spectrum, the presence or absence of the following points must be taken into account: a strong adsorption in the $1\,630-1\,550\,cm^{-1}$ range, due to a skeletal stretching vibration, a strong thiocarbonyl stretching band near $1\,140\,cm^{-1}$ and finally, an N–H stretching band[1-3].

Moreover, the study of hydrogen bonds in these compounds is important owing to the possible formation of intermolecular associations which give rise to either very stable linear oligomers with a relatively high average degree of polymerization or cyclic dimer species[4].

In this work, the vibrational, infrared and Raman, spectra of 2-mercaptoimidazole and 2-mercaptothiazole have been studied. For the first one, the i.r. spectra in solid state, in methylimidazole solution as well as the solid Raman spectrum have been recorded. For 2-mercaptothiazole the i.r. and Raman spectra in solid state as well as the i.r. spectra in CS_2 and $CHCl_3$ 0·05M solutions have been studied.

The aim of the present work was to investigate the vibrational spectrum of these compounds. The proposed assignments for thiazole[5] and imidazole[6,7], the vibrational study of 2-mercaptothiazole carried out by Mille et al.[8], the possible existence of tautomerism between the mercapto-form and the thione-form, and finally the presence of intermolecular associations by hydrogen bonding have been taken into account.

EXPERIMENTAL

The samples used were 2-mercaptoimidazole with 98% purity and 2-mercaptothiazole with over 97% purity both from Aldrich and were used without further purification.

Infrared spectra were recorded on a Perkin–Elmer 783 spectrophotometer in the 4 000—200 cm^{-1} range. Results for the solutions in $CHCl_3$, CS_2 and 1-methylimidazole were obtained with cells of different path lengths fitted with CsI and KBr windows. Standards for wavenumber determinations were polystyrene film and indene–camphor–cyclohexanone mixtures as described in ref.[9]. The Raman spectra were taken on a Jobin Yvon U-1000 spectrometer using the 5 145 Å exciting line of a Spectra Physics 2020 Ar^+ laser. The experimental values, together with proposed assignements, are summarized in Tables I and II.

RESULTS AND DISCUSSION

2-Mercaptoimidazole

The vibrational analysis of the i.r. and Raman spectra, which will be discussed next, has allowed us to assume that the mercapto-form is the main tautomer form present, due to the presence in the spectrum of bands assigned to the SH group and to the absence of bands characteristic of the C=S group. Thus, assuming a planar structure for the molecule, and therefore belonging to the C_s symmetry group, the twenty-four normal vibration modes must be active in the i.r. as well as the Raman spectra. Of these vibrations, 17 must be of A' symmetry specie and 7 of the A'' symmetry specie. Molecular vibrations were divided up for study into three groups: ring vibrations, CH and NH vibrations and vibrations of the SH group.

Ring vibrations. The vibrations of imidazole and derivatives have been studied in detail prior to this work. The vibrations W_2, W_3, W_5, W_6 and W_7; A' have been recorded in both solid and solution i.r. and Raman spectra, while W_1; A', W_4; A', Γ_1; A'' and Γ_2; A'' have only been observed in the i.r. spectra. The frequencies of these vibrations are shown in Table I, apparently unchanged with respect to the values for imidazole. Only W_1 and W_4 have been recorded at higher and lower values, respectively, than for imidazole although the same band structure is maintained.

CH *and* NH *vibrations*. The stretching vibrations of the CH bonds in positions 4 and 5 whether vibrating together in phase or not, have been recorded at 3 144·8 cm^{-1} and 3 124·2 cm^{-1}, while the in-plane deformation vibrations $\delta(CH)$ have been recorded in the solid i.r. spectrum at 1 226·6 cm^{-1} and 1 073·1 cm^{-1}. The out-of-plane deformation vibrations $\gamma(CH)$ appear at 780·0 cm^{-1} and 737·4 cm^{-1} only in the solid i.r. spectrum. In all cases, there is a good correlation with those obtained for imidazole.

Regarding the NH group, a band structure similar to that of imidazole in the 3 000 cm^{-1} range is seen, with a central maximum at 2 862 cm^{-1}, and thus a strong intermolecular hydrogen bonding between the NH group of imidazole and the nitro-

TABLE I

Summary of frequencies and assignments in infrared and Raman spectra of 2-mercaptoimidazole

Solid i.r.		Solid Raman		Assignment
I	ν	I	ν	
m^a	275			$\gamma(S\text{–}H);\ A''$
m	346·8			$\delta(C\text{–}S);\ A'$
m	602·8			$\Gamma_2;\ A''$
vs	675·1			$\Gamma_1;\ A''$
m	687·3			$\nu(C\text{–}S);\ A'$
vs	737·4			$\gamma_2(CH);\ A''$
s	780·0			$\gamma_1(CH);\ A''$
w	842·2			$\delta(S\text{–}H) + \delta(C\text{–}S);\ A'$
m	872·7	vw	880·5	$W_7;\ A'$
s	912·0	w	916·2	$W_6;\ A'$
w	955·0	w	953·1	$\gamma(NH);\ A''$
vs	1 073·1			$\delta_2(CH);\ A'$
sh	1 108·7			$2\,W_5 - W_5;\ A'$
m	1 123·7	m	1 117·4	$W_5;\ A'$
w	1 144·8	m	1 136·7	$\delta(NH);\ A'$
sh	1 218·9			$W_7 + \delta(C\text{–}S);\ A'$
vs	1 226·6	m	1 227·9	$\delta_1(CH);\ A'$
s	1 266·6			$W_4;\ A'$
w	1 357·9			$2\,\nu(C\text{–}S);\ A'$
m	1 404·9			$\gamma_2(CH) + \Gamma_1;\ A''$
m	1 421·9	vw		$W_3;\ A'$
sh	1 471·5			$2\,\gamma_2(CH);\ A'$
vs	1 477·8	m	1 477·7	$W_2;\ A'$
sh	1 559·8			$2\,\gamma_1(CH);\ A'$
sh	1 572·8			$W_6 + \Gamma_1;\ A''$
vs	1 586·1			$W_1;\ A'$
w	1 684·0			$W_6 + \gamma_1(CH);\ A''$
w	1 732·7			$2\,W_7;\ A'$
w	2 135·6			$2\,\delta_2(CH);\ A'$
w	2 234·1			$2\,W_5;\ A'$
				$W_3 + W_7;\ A'$
w	2 285·4			$2\,\delta(NH);\ A'$
w	2 379·6			$W_2 + W_6;\ A'$
				$W_4 + W_5;\ A'$
w	2 491·7			$W_1 + W_6;\ A'$
				$W_4 + \delta_1(CH);\ A'$
m	2 531·9			$\nu(S\text{–}H);\ A'$
m	2 631·9			$W_3 + \delta_1(CH);\ A'$
m	2 694·3			$W_2 + \delta_1(CH);\ A'$
m	2 740·8			$W_2 + W_4;\ A'$

TABLE I

(*Continued*)

Solid i.r.		Solid Raman		Assignment
I	ν	I	ν	
m	2 804·0			$W_1 + \delta_1(CH)$; A'
s	2 862·4	w	2 860·7	$\nu(NH)$; A'
s	2 981·2			$W_1 + W_3$; A'
vs	3 124·2	w	3 120·6	$\nu_2(CH)$; A'
s	3 144·8	w	3 136·2	$\nu_1(CH)$; A'

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

gen atom in position 3 of another imidazole molecule is assumed (Fig. 1a). The $\delta(NH)$ vibration which was assigned for imidazole to the strong characteristic band in the Raman spectrum at 1 190·5 cm^{-1}, is assigned to the weak band in the i.r. spectrum which appears at 1 144·8 cm^{-1}, while the band at 955·0 cm^{-1} is assigned to the corresponding $\gamma(NH)$. In the Raman spectrum they appear at 1 136·7 cm^{-1} and 953·1 cm^{-1}, respectively.

Vibrations of the substituent. The presence of the bands corresponding to the CSH grouping and the absence of bands that could be assigned to the C=S group have allowed us to confirm a mercapto-form for the molecule being studied. The SH stretching mode has been assigned to a weak band in the solid i.r. spectrum at 2 532·6 cm^{-1}, which falls in the range predicted by the various research work for this mode[10]. Likewise, the bands at 518·0 cm^{-1} and 275 cm^{-1} have been assigned to the corresponding in-plane and out-of-plane SH bending vibrations.

The stretching of the C—S bond has in all cases been assigned as a band which is found in the 720 – 570 cm^{-1} range[10], of weak or medium intensity in the i.r. spectrum and very strong in the Raman spectrum. In our study, this band is recorded at 687·3 cm^{-1} in the i.r. spectrum and as the strongest band in the Raman spectrum at 692·7 cm^{-1}. The corresponding in-plane C–S deformation is assigned at 346·8 cm^{-1}, the band corresponding to $\gamma(C-S)$ not having been observed on either recording. In no case have bands which could be assigned to the C=S group been observed.

2-Mercaptothiazole

For 2-mercaptothiazole, a thione form (Fig. 1b) in both the solid state and solvent of low polarity as well as the existence of an intermolecular dimer association by

hydrogen bonding in the solid state involving the formed N—H and C=S group (Fig. 1c) have been assumed, in agreement with other similar molecules[1,2,8,11] and with ^{13}C n.m.r. data[12]. However, when the i.r. spectra in dilute solutions of inert solvents are investigated, the break of the previously mentioned association is found. Taking into account this fact, when the spectrum is studied, a C_s symmetry group is assumed, i.e., symmetry of an isolated molecule. The features which enable us to adopt these conclusion are: First, the presence in the CS_2 solution i.r. spectra of a band at $3\,408 \cdot 3\ cm^{-1}$ which has been assigned to the NH stretching vibration in unassociated molecules. In the solid i.r. spectra, this band is not found and the presence of a strong and broad band centered around $2\,887\ cm^{-1}$, a band structure
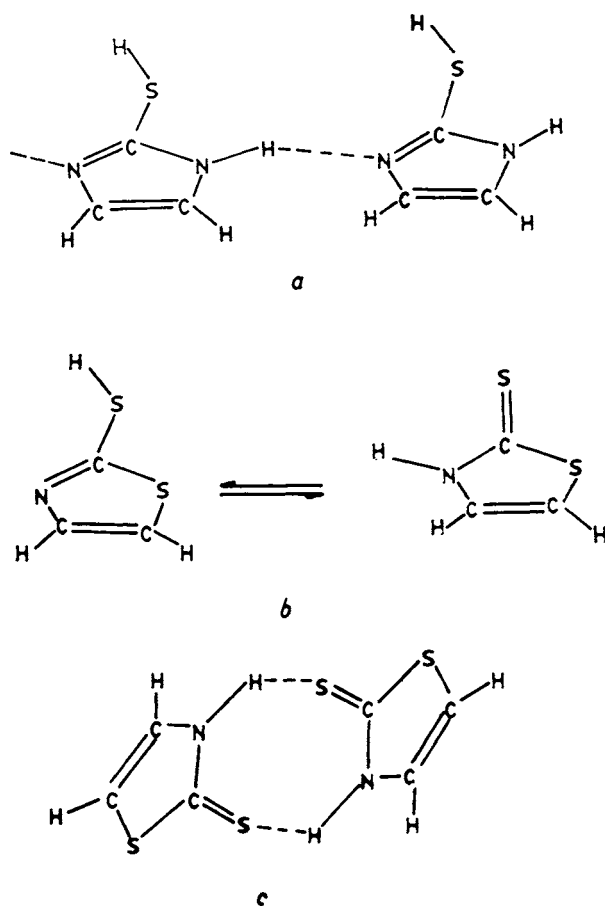

FIG. 1

Associations and tautomerism in the 2-mercaptoimidazole (a) and 2-mercaptothiazole (b) and (c) molecules

TABLE II

Summary of frequencies and assignments in infrared and Raman spectra of 2-mercaptothiazole

Solid i.r.		Solution[b] i.r.		Solid Raman		Assignment
I	v	I	v	I	v	
m[a]	296·2			s	275	$\gamma(C{=}S)$; A''
s	466·8	s	464·7	m	460	$\delta(C{=}S)$; A'
s	492·4	s	495·0	w	495	Γ_2; A''
m	580·0	w	580·9			Γ_1; A''
s	640·9	s	644·8	s	640	W_7; A'
vs	684·9	s	683·5			$\gamma_2(CH)$; A''
vs	703·2	m	758·4			$\gamma(NH)$; A''
s	782·2	m	726·1	vw	727	W_6; A'
sb	794·8	vs	780·2			$\gamma_1(CH)$; A''
vs	846·0	vs	846·4	w	843	W_5; A'
m	873·1		874·7	vw	873	W_4; A'
vw	922·6					$2\,\delta(C{=}S)$; A'
vs	1 048·4	vs	1 045·2	w	1 045	$\delta_2(CH)$; A'
vs	1 069·9	m	1 066·4	w	1 068	$\delta_1(CH)$; A'
s	1 136·9	s	1 136·0	w	1 136	$\nu(C{=}S)$; A'
m	1 154·7					$2\,\Gamma_1$; A'
vw	1 194·4					$W_6 + \delta(C{=}S)$; A' $\Gamma_2 + \gamma(NH)$; A'
vs	1 240·6	m	1 240·0	m	1 241	W_3; A'
w	1 270·2					$2\,W_7$; A'
vw	1 282·7					$\Gamma_1 + \gamma(NH)$; A'
s	1 332·9	s	1 332·8	m	1 332	W_2; A'
sh	1 380·9	sh	1 390·4			$\gamma_2(CH) + \gamma(NH)$; A'
m	1 405·2					$2\,\gamma(NH)$; A'
vs	1 457·4	s	1 461·2	m	1 459	$\delta(NH)$; A'
vs	1 548·8	s	1 553·7	w	1 549	W_1; A'
m	1 745·4					$2\,W_4$; A'
m	1 765·4					$W_6 + \delta_2(CH)$; A'
m	2 060·9	vw	2 067·2			$W_3 + W_6$; A'
w	2 302·8	vw	2 305·3			$\delta_1(CH) + W_3$; A'
w	2 523·1	w	2 523·1			$\delta(NH) + \delta_1(CH)$; A'
w	2 589·6	w	2 589·2			$\delta(NH) + \nu(C{=}S)$; A'
m	2 698·0	m	2 698·8			$\delta(NH) + W_3$; A'
m	2 785·2	m	2 789·2			$W_2 + \delta(NH)$; A'
s	2 887·0	w	2 887·3			$\nu(NH)_{ass.}$; A'
s	2 973·3	s	2 978·3			$W_1 + \delta(NH)$; A'
sb	3 059·9	vs	3 071·1			$\nu_1(CH)$; A'
sb	3 110·7	vs	3 123·4	w	3 117	$\nu_2(CH)$; A'
		m	3 408·3			$\nu(NH)_{free}$; A'

[a] Notation taken from Table I; [b] the frequencies given in the $4\,000-2\,300$ cm^{-1} and $900-600$ cm^{-1} regions are values in CS_2 0·05M solutions.

which is similar to the one observed for the imidazole and 2-mercaptoimidazole molecules, has been assigned to the NH group with hydrogen bonds in a dimer structure. The band in the solution i.r. spectrum at 1 469·2 cm^{-1} which appears in the solid i.r. spectrum at 1 457·4 cm^{-1} and similar value in the Raman spectrum has been assigned to the corresponding in-plane N–H bending vibration coupled with the W_1 and W_2 ring modes which appear to higher and lower values, respectively than in the thiazole molecule, in agreement with the assignment made by Mille et al.[8] The out-of-plane N–H bending vibration appears close to 750 cm^{-1}, region where the out-of-plane CH deformation and ring vibrations appear. The bands at 780·2 cm^{-1} and 758.4 cm^{-1} in the i.r. spectrum of 0·05M-CS$_2$ solution, which appear at 794·8 cm^{-1} and 703·2 cm^{-1}, the latter not resolved by Mille et al.[8], but clearly resolved in our solid i.r. spectrum, have been assigned to the $\gamma(CH)$ and $\gamma(NH)$ respectively, possibly coupled. This displacement of frequency values, meanly for the $\gamma(NH)$ vibration, can be explained taking into account the break of the dimer structure in CS$_2$ solution.

Secondly, the presence of a strong band in the i.r. spectrum near 1 140 cm^{-1} is proof of the presence of a thiocarbonyl group, corresponding to the C=S stretching vibration[1]. For 2-mercaptothiazole, this band is observed at 1 136·9 cm^{-1} in both the solid and solution i.r. spectra, which appears in the Raman spectrum at 1 131 cm^{-1}. The bands which appear at 466·8 cm^{-1} and 296·2 cm^{-1} in the solid i.r. spectrum and at similar values in the solution i.r. and solid Raman spectra are assigned to the corresponding in-plane and out-of-plane deformation in the C=S bond.

Finally, the presence of a very strong band at 1 550 cm^{-1}, a frequency higher than one observed for the aromatic skeletal motion W_1 in the thiazole base molecule, has been assigned in all cases due to a strong vibrational coupling of the —N—C=S group[1].

In no case have bands that might be assigned to the S--H group been observed, and thus we may conclude that this substance is thione.

The remaining vibrations in this molecule are summarized in Table II, and are chiefly based on a correlation with the thiazole spectra[5] and with those of other thiocarbonyl aromatic compounds.

Some generally weak bands recorded for both compounds in the solid and solution i.r. spectra have been assigned as a combination, overtone or difference band, and their assignments are shown in Tables I and II.

Thermodynamic Functions

The thermodynamic functions C_p^0/R, $(H-H_0)/RT$, S^0/R and $-(F-H_0)/RT$ for 2--mercaptoimidazole and for 2-mercaptothiazole have been computed for 21 temperatures in the 200 − 1 400 K range, making use of the assignments in solution of the

TABLE III

Thermodynamic functions calculated for 2-mercaptothiazole and 2-mercaptoimidazole in the ideal gas state at 101·3 kPa (in J mol^{-1} K^{-1})

T, K	2-Mercaptothiazole				2-Mercaptoimidazole			
	C_p^0/RT	$(H-H_0)/RT$	$-(F-H_0)/RT$	S^0/R	C_p^0/R	$(H-H_0)/RT$	$-(F-H_0)/RT$	S^0/R
200·0	6·85	4·78	28·42	33·20	7·85	5·61	28·85	34·46
250·0	8·45	5·35	29·55	34·90	9·34	6·20	30·17	36·37
300·0	10·03	6·01	30·58	36·58	10·88	6·85	31·36	38·21
350·0	11·48	6·68	31·56	38·24	12·35	7·54	32·46	39·99
400·0	12·78	7·36	32·49	39·86	13·71	8·22	33·52	41·74
450·0	13·92	8·03	33·40	41·43	14·93	8·90	34·52	43·43
500·0	14·91	8·78	34·28	42·95	16·02	9·56	35·49	45·06
550·0	15·77	9·28	35·14	44·41	16·99	10·19	36·44	46·63
600·0	16·52	9·85	35·97	45·82	17·85	10·80	37·35	48·15
650·0	17·18	10·39	36·78	47·17	18·62	11·37	38·24	49·60
700·0	17·76	10·89	37·57	48·46	19·31	11·91	39·10	51·01
750·0	18·28	11·37	38·33	49·70	19·93	12·42	39·94	52·36
800·0	18·74	11·82	39·08	50·90	20·49	12·91	40·76	53·67
850·0	19·16	12·24	39·81	52·05	21·00	13·37	41·55	54·93
900·0	19·54	12·63	40·52	53·15	21·46	13·81	42·33	56·14
950·0	19·89	13·01	41·21	54·22	21·89	14·22	43·09	57·31
1 000·0	20·21	13·36	41·90	55·25	22·27	14·62	43·83	58·45
1 050·0	20·49	13·69	42·55	56·24	22·63	14·99	45·55	59·54
1 100·0	20·77	14·01	43·20	57·20	22·96	15·35	45·25	60·60
1 200·0	21·23	14·59	44·44	59·03	23·53	16·01	46·62	62·62
1 400·0	21·98	15·59	46·77	62·36	24·15	16·89	47·98	64·79

fundamental vibration frequencies for the free species proposed in this work and by assuming a rigid-rotor, harmonic-oscillator model for the ideal-gas state at a pressure of 101·3 kPa. The rotational constants were computed using the structural parameters given in refs[13−15]. The symmetry number used was 1. Table III provides a summary of these thermodynamic functions.

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