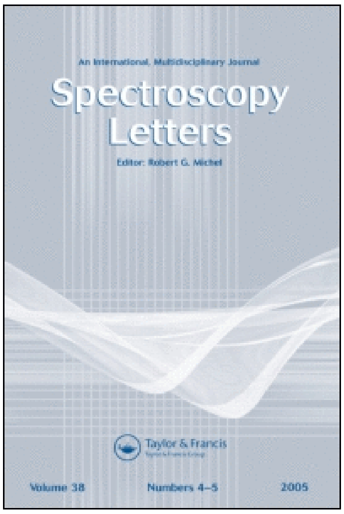

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Vibrational Spectra of Benzimidazol-2-Thione

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VIBRATIONAL SPECTRA OF BENZIMIDAZOL-2-THIONE

Key words: infrared, Raman, polarized spectra,
benzimidazol-2-thione

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ABSTRACT

The i.r. spectra of benzimidazol-2-thione have been measured from 4000 to 180 cm^{-1}; polarized spectra of single crystals have been also obtained. The Raman spectra of polycrystalline samples and solutions have been recorded and the polarization of many lines has been determined. Most vibrations have been assigned on the basis of the i.r. dichroism, Raman spectra and correlative arguments.

INTRODUCTION

Benzimidazole derivatives have been tested as inhibitors of corrosion of metals and alloys under different environment conditions [1-5]. In particular, benzimidazol-2-thione (BZIMT in the following) proved effective in slowing the dissolution of C-steel in acidic media [2] and the corrosion of brass in alcaline solutions [3]; moreover, it has protective effects for copper, brass and aluminium in saline solutions [4] and for aluminium brass in neutral aqueous solutions [5]. The inhibitory effects have been related to the formation of a protective layer of coordinated molecules at the surface of the metal [6]. The study of the vibrational spectra of metal complexes of BZIMT can provide information about the coordination mechanism of this molecule at the metal surface : however, to give a correct interpretation of the spectral data for the complexes, a detailed vibrational analysis of the ligand molecule is essential. It appears that only a discussion of a limited number of the infrared bands of BZIMT has been reported in the literature [7,8,9]. The aim of the present study is to provide an extension of the vibrational assignment on the basis of the i.r. dichroic measurements on single crystals and Raman spectra.

EXPERIMENTAL

Commercial BZIMT was purified by repeated crystallizations. N-deuterated samples were prepared by repeated exchanges with D_2O/MeOD. Single crystals were grown by slow evaporation of methanol solutions. X-ray methods showed that the well developed face of the crystals used in absorption measurements contained the a and b axes. The i.r. spectra were recorded with Perkin-Elmer 225 and 983G spectrophotometers. Polycrystalline samples were in the form of KBr pellets and Nujol mulls. Polarized i.r. spectra of single crystals were obtained using a wire-grid polarizer and a reflecting beam-condenser. The Raman spectra were obtained with a SPEX "Ramalog" instrument using the 647.1 nm line of a Spectra-Physics model 165 Kr^+ laser for the excitation. Depolarization ratios were also determined for some bands from methanol solutions.

RESULTS AND DISCUSSION

Selection Rules and Spectral Predictions

Crystals of BZIMT are monoclinic, space group $P2_1/m$ (C_{2h}^2), with two molecules of C_{2v} symmetry in the unit cell, located on C_s sites [6]. The molecules are connected by hydrogen bonds forming extended chains along the b axis. The selection rules for the BZIMT molecules and the crystal are summarized in Table 1. It turns out from this table that the i.r. inactive A_2 molecular modes should gain activity in the solid state and each molecular fundamental should give two components in the crystal spectra, one i.r. active and one Raman active. In particular, the i.r. components coming from the A_2 and B_2 modes should prove polarized

TABLE 1

Selection rules for the free molecule and the unit cell of Benzimidazol-2-thione

Molecule C_{2v}	Site C_s	Unit cell C_{2h}
A_1 15 (i.r.,R)		A_g 25 (3L) (R)
A_2 6 (R)	A' 22 (i.r.,R)	B_g 23 (3L)
B_1 7 (i.r.,R)	A" 20 (i.r.,R)	A_u 22 (2L)+T_b (i.r.)
B_2 14 (i.r.,R)		B_u 23 (1L)+T_{ac} (i.r.)

L=Lattice modes

along the <u>b</u> axis and those coming from the A_1 and B_1 vibrations in the <u>ac</u> plane. The proportionality factors for the i.r. band intensities in the oriented gas approximation, collected in Table 2, suggest that the A_1 vibrations should exhibit the same dichroic behaviour as the B_1 modes in the polarized spectra recorded on the <u>ab</u> crystal plane.

Therefore, segregation of the A_1 vibrations may be attempted with the aid of the Raman data.

Vibrational assignments

The relevant i.r. and Raman data are collected in Table 3 together with the assignments.

The strong i.r. band centred at ~3150 cm^{-1} which moves to 2350 cm^{-1} on deuteration may be associated to

TABLE 2

Proportionality factors for oriented gas band intensities of Benzimidazol-2-thione

	a	b	$c^*(\perp ab)$
A_1	0.4809	0.0	0.5189
B_2	0.0	1.0	0.0
B_1	0.5189	0.0	0.4809

the NH stretching fundamentals. The behaviour in polarized light suggests that the maximum at 3150 cm^{-1} corresponds to the mode of B_2 species, while the peak at 3110 cm^{-1} is attributable to the totally symmetric vibration. The region of the CH stretching fundamentals is obscured by the tail of the strong NH absorption. A CH stretching mode of B_2 species may be associated to the b-polarized component at 3050 cm^{-1}, whereas the totally symmetric modes are assigned to the Raman lines at 3074 and 3034 cm^{-1}.

The polarized Raman lines appearing at 1462, 1279, 1199, 1020, 971, 819 and 419 cm^{-1}, which correspond to a-polarized bands in the i.r. spectrum, can be easily assigned to seven totally-symmetric fundamentals. It is worth pointing out that the assignament of the band at 419 cm^{-1} to a skeletal mode with strong C=S stretching character, proposed by previous authors

TABLE 3

Experimental spectral data and assignments for Benzimidazol-2-thione

i.r. frequencies and polarization			Raman shift and polarization		Assignment	
3240	sh	b			B_2	
3150	vs	b			B_2	ν NH
3110	s	a			A_1	ν NH
3090	sh	(a)	3074	vw	A_1	ν CH
3050	m	(b)			B_2	ν CH
			3034	vw	A_1	ν CH
1624	w	a	1624	vw	A_1	ν skeletal
1616	sh	a			A_1	
1594	vw*	a			A_1	
1579	w*	b			B_2	ν skeletal
1511	vs	a	1501	w	A_1	ν skeletal, δ NH
1466	m	a	1462	ms(p)	A_1	ν skeletal
1450	w*	b			B_2	ν skeletal
1410	vw	a			A_1	
1390	sh	b			B_2	
1375	m	b			B_2	δ NH, ν skeletal
1356	ms	b>a	1356	vw	A_1/B_2	ν skeletal
1338	mw	b>a			B_2/A_1	ν skeletal
1270	w	a	1279	ms(p)	A_1	ν skeletal
1258	m	b			B_2	δ CH
1239	w	a	1234	w	A_1	ν skeletal
1213	m	b			B_2	ν skeletal
1177	vs	a	1199	ms(p)	A_1	δ CH
1169	m*	b	1164	vw	B_2	ν skeletal
1106	w*	b	1117	vw	B_2	δ CH
1057	vw	b			B_2	δ, ν skeletal
1014	mw	a	1020	m(p)	A_1	δ CH, ν skeletal
998	sh	b			B_2/A_2	
976	w	a	971	m(p)	A_1	δ skeletal
961	vw*	b	963	vw	A_2	τ CH
952	vw*	a			A_1/B_1	
919	m	a			B_1	τ CH
898	vw	b			A_2/B_2	
885	vw	b			A_2/B_2	
			868	w	A_2	τ CH
813	vw	a	819	m(p)	A_1	δ skeletal

Table 3 (continued)

i.r. frequencies and polarization			Raman shift and polarization		Assignment	
741	vs	a			B_1	τ CH
705	s,br	a			B_1	τ NH
	**	)				
659	ms	a			B_1	τ skeletal, τ NH
614	w	b	619	m(?)	B_2	δ skeletal
601	s	a	603	mw	A_1	δ skeletal
			570	vw	A_2	τ skeletal
481	m	b			B_2	δ skeletal
429	mw	a			B_1	τ skeletal
417	m	a	419	ms(p)	A_1	ν (C=S), δ skeletal
321	vw	a	322	w(p?)	A_1	δ skeletal
264	mw	b			B_2	
		}	271	w(dp)	}	δ skeletal
253	w	b			B_2	
					A_2	
			235	w(dp?)	{ B_1 }	τ,δ skeletal
					B_2	
			133	m		lattice
			112	s		lattice
			94	vs		lattice
			54	m		lattice

* Observed only in the single crystal spectrum
** Evans hole
a: bands polarized parallel to the a crystal axis
b: bands polarized parallel to the b crystal axis
s=strong, m=medium, w=weak ; p=polarized, dp=depolarized
ν=stretching, δ=in-plane bending, τ=out-of-plane bending

with the aid of selenation techniques [9], is in agreement with the Raman and dichroic data presented in this work. The band at 321 cm^{-1} is recognized as an A_1 fundamental on the basis of the dichroism, the depolarization ratio being uncertain. Also the choice

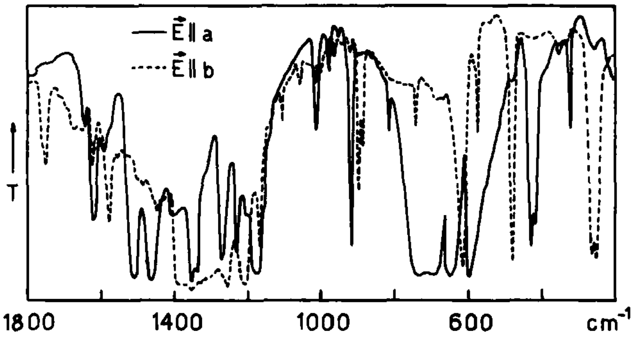

Fig. 1. Polarized i.r. spectrum of benzimidazol-2-thione, ab crystal plane

of the Raman bands at 1624, 1501, 1234 and 603 cm^{-1} as A_1 fundamentals is supported mainly by the dichroism of the corresponding i.r. bands. The assignments proposed in the literature for benzimidazole [10,11] suggest the presence of a totally symmetric skeletal stretching mode between 1400 and 1300 cm^{-1}. As a matter of fact the absorption bands observed in this range show a prevailing polarization along the _b_ axis, characteristic of the B_2 modes. However, one Raman line is found at 1356 cm^{-1}, although with very low intensity, and _a_-polarized components, with maxima at 1356 and 1338 cm^{-1}, are clearly observed in the i.r. spectra. In the light of the above facts, a fundamental of A_1 species can be tentatively located at 1356 cm^{-1}.

The clear polarization along the _b_-axis makes straightforward the assignment of the absorption bands at 1579, 1375, 1258, 1213, 614, 481 and 264-253 cm^{-1} to B_2 fundamentals. As discussed above, the prevailing b-polarization of the i.r. bands between 1370 and 1300 cm^{-1} marks the presence of B_2 modes. The bands at 1356 and 1338 cm^{-1} seem equally plausible candidates for the B_2 fundamental which is expected in this range on correlative basis [10]: however, bearing in mind the assignments for the A_1 modes, the choice of the latter band seems preferable. Correlative arguments based on the assignaments of benzimidazole [10,11] suggest that three other fundamentals of B_2 symmetry should be located above 1000 cm^{-1}. These modes may be tentatively associated to the weak b-polarized components observed at 1450, 1169 and 1106 cm^{-1} in the single crystal spectra: the presence of the weak Raman lines at 1164 and 1117 cm^{-1} corroborates the choice for the last two modes.

The available data do not allow an univocal assignment of the in-plane NH bending modes. In fact, deuteration affects several absorption bands between 1600 and 1100 cm^{-1}, that is diagnostic of some NH in-plane bending character for several fundamentals.

On correlative grounds [12], the a-polarized i.r. bands at 919 and 741 cm^{-1} may be safely assigned to the CH out-of-plane bending fundamentals of B_1 species, whereas the a-type polarization of the broad band at

705 cm^{-1}, which moves to 501 cm^{-1} on deuteration, confirms the attribution to the B_1 NH out-of-plane fundamental proposed by previous authors [9]. Likewise, the dichroism suggests the assignment to the B_1 symmetry for the bands at 659 and 429 cm^{-1}, for which no counterpart is observed in the Raman spectrum.

Two CH out-of-plane fundamentals of A_2 symmetry are predicted near 970 and 850 cm^{-1} by correlative arguments [12]. The _b_-polarized absorption observed with low intensity at 961 cm^{-1} in the single crystal spectrum, which corresponds to the weak Raman line at 963 cm^{-1}, may be assigned to the highest frequency mode, whereas the Raman band at 868 cm^{-1}, without i.r. counterpart, is associated to the remaining τCH fundamental. Likewise, the weak Raman band at 570 cm^{-1} represents a plausible candidate for the assignment of a skeletal deformation mode of A_2 symmetry since no corresponding absorption is found in the infrared. At last, the depolarized character suggest the attribution of the weak Raman band at 235 cm^{-1} to a non totally-symmetric skeletal deformation mode, but the assignment can be specified no further on the basis of the presently available data.

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