

Infrared and Raman Spectra of Benzimidazole

A. Suwaiyan,* R. Zwarich† and N. Baig

Laser Research Laboratory and Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Polarized IR spectra of partially oriented benzimidazole crystals grown from the melt pressed between salt plates were recorded. The depolarization ratios of the Raman bands in the melt and the polarized Raman spectra of a single crystal in all possible orientations were measured. The experimental assignment of the fundamental vibrational bands is compared with a set of calculated values.

INTRODUCTION

This work is part of a continuing study on the vibrational spectroscopy of heterocyclic aromatic rings. In a previous study, we reported the vibrational spectra of indole.¹ In this paper, we report a study of benzimidazole, with two nitrogen atoms. The IR spectra of solid benzimidazole have been reported.²⁻⁴ However, it appears that no work has been published on the polarized spectra of the molecule in the melt or as the single crystal.

In this study, we recorded the polarized IR and Raman spectra of benzimidazole in order to assign the molecular fundamental vibrations.

EXPERIMENTAL

Benzimidazole (Fluka) was used after repeated vacuum sublimation to remove particulate and coloured impurities. Thin, partially oriented samples suitable for IR spectroscopy were prepared by cooling melted benzimidazole pressed between tightly held potassium bromide discs. Polarized IR spectra were recorded with a Perkin-Elmer gold-wire grid polarizer and a Perkin-Elmer Model 180 spectrometer.

The Raman spectra were obtained with a Spex Ramalog 5 spectrometer fitted with a Spectra-Physics Model 165 argon ion laser. The power of the 514.5-nm radiation at the sample was 900 mW and the spectral slit width was 2 cm^{-1} . The benzimidazole sample used for the solution investigated was sealed in an evacuated Pyrex tube and heated so that the melt remained in contact with some solid (m.p. 172.5°C). Raman spectra of a large single crystal grown in a Bridgman furnace were also recorded. The benzimidazole crystals were cut along the crystallographic directions, which were identified from the optical properties.⁵

CRYSTAL STRUCTURE

Two independent benzimidazole crystal structure determinations^{5,6} showed good agreement. Since the studies used different axes conventions, we have chosen to use the space group $Pna2_1$. Benzimidazole crystallizes with four molecules in an orthorhombic unit cell in which each molecule is associated with two neighbouring molecules through hydrogen bonding. The length of the hydrogen bond between the hydrogen and the nitrogen of the neighbouring molecule is 2.00 \AA . The carbon and nitrogen atoms define a plane.⁶ Figure 1

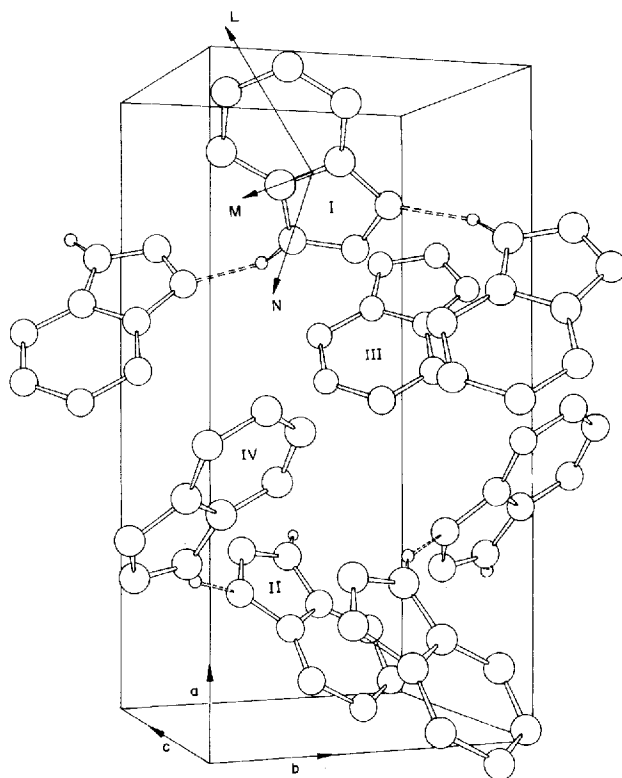


Figure 1. The benzimidazole unit cell. An axis frame (L , M , N) has been placed on molecule I. Axis frames on molecules II, III and IV in the unit cell are generated by the space group operations C_2^c , σ_v^{bc} and σ_v^{ac} , respectively. The hydrogen atom (shown as the small circle) attached to the nitrogen atom at position 1 in the five-membered ring is the only one shown.

* Author to whom correspondence should be addressed.

† Present address: Chemistry Department, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6.

Table 1. Square of the direction cosines of the molecular axes *L*, *M* and *N* with respect to the crystal axes *a*, *b* and *c*

Molecular axis	Crystal axis		
	<i>a</i>	<i>b</i>	<i>c</i>
<i>L</i>	0.080	0.510	0.410
<i>M</i>	0.520	0.361	0.119
<i>N</i>	0.399	0.132	0.469

shows the molecular structure and the choice of the molecular axes. The direction cosines relating the crystal axes and the molecular axes are given in Table 1 and the selection rules for transitions in the free molecule and in the crystal are given in Table 2.

The optical data for the benzimidazole crystal have been summarized by Winchell.⁷ Ingots grown by the Bridgman method clearly showed the perfect *bc* cleavage plane. Since the *bc* plane is the optic axial plane and the *b* axis is parallel to the acute bisectrix, the crystallographic directions were easily identified. The prominent face of sublimation flakes and platelets grown from the melt pressed between silica is also the *bc* plane; although their long direction does not, in general, correspond to a crystallographic direction, the acute bisectrix (*b* axis) usually does have a large projection along it.

SPECTRA

The IR spectrum of partially oriented benzimidazole crystals grown from the melt pressed between salt plates and recorded in polarized light is shown in Fig. 2. Since the *b* axis is parallel to the acute bisectrix, only those bands clearly most intense along the *b* axis have been marked $\parallel b$ in Table 3. The depolarization ratios of the Raman lines were measured in the melt. These values together with the band intensities and frequencies are listed in Table 3. A literature survey of the work on benzimidazole is also included in Table 3. The spectrum of the melt is shown in Fig. 3. Representative Raman spectra of the benzimidazole crystal are reproduced in Fig. 4(a) and (b).

The four benzimidazole molecules in the unit cell are expected to generate 21 lattice modes, all of which are Raman active in a unit cell with C_{2v} factor group symmetry and zero wavevector. In our spectra at room temperature, the low-frequency Raman bands are not resolved well enough to account for the number and

symmetry of the lattice modes. A comparison of the melt spectra with the solid spectra is used to exclude lattice modes from the study.

Since the benzimidazole molecule has only C_s symmetry, all 39 molecular vibrations are both IR and Raman active. Excluding the C–H and N–H stretching vibrations, the remaining 33 vibrations are expected to have frequencies below 2000 cm^{-1} . Of these, 21 in-plane vibrations correspond to polarized bands with A' symmetry and 12 out-of-plane vibrations correspond to polarized bands with A'' symmetry. The symmetry assignments given in Table 3 are based on a comparison of the IR and Raman spectra. The oriented gas model predicts the IR-active vibrations with A' symmetry will be most intense parallel to the *b* axis whereas A'' -type vibrations will be most intense parallel to the *c* axis. The polarization information from the well resolved Raman spectra of the single crystal is used to identify nearly degenerate modes that would appear as essentially single bands in the melt spectrum. For example, the poorly resolved doublet in the melt Raman spectrum at 1349 and 1368 cm^{-1} splits into two sharp bands in the crystal.

Nine out-of-plane vibrations with A'' symmetry are clearly located at 424 , 578 , 628 , 740 , 760 , 848 , 880 , 890 and 929 cm^{-1} in the IR spectrum of the crystal.

The 637 cm^{-1} is not clearly resolved from the 628 cm^{-1} band in the IR spectrum. These bands are, however, clearly resolved in the crystal Raman spectrum. The 637 cm^{-1} band is assigned to a torsion in the imidazole part of the molecule because of its appearance in the spectra of imidazole and benzimidazole and some of their derivatives.²

In the $700\text{--}800\text{ cm}^{-1}$ region, the 740 cm^{-1} is shifted by deuteration² at the 1- and 2-positions on the imidazole ring whereas the 760 cm^{-1} is not affected by the substitution. Hence the 760 cm^{-1} band can be correlated with the in-phase out-of-plane hydrogen wags and the 740 cm^{-1} band with the imidazole ring γCH motion. Similarly, bands at 628 cm^{-1} and 848 cm^{-1} can be assigned to out-of-plane modes for the NH and CH groups, respectively. The 424 cm^{-1} band is assigned to torsion in the benzene ring.

The skeletal modes giving rise to prominent Raman bands closely resemble their benzene and imidazole ring counterparts. The 1589 and 1620 cm^{-1} bands seem to correlate with the benzene e_{2g} band at 1596 cm^{-1} . In this case the doubly degenerate band of benzene is split on lifting the degeneracy to give two bands at 1596 and 1620 cm^{-1} . Similarly, the doubly degenerate band of benzene at 1482 is split in benzimidazole to give two

Table 2. Correlation table for benzimidazole showing the selection rules for the isolated molecule and the crystal^a

Molecular point group C_s			Factor group C_{2v}			
Z	Selection rules, molecular bases	Symmetry	Site group C_1 : symmetry	Symmetry	Selection rules, molecular bases	n
27	LL, MM, NN, LM	A'	A	a_1	aa, bb, cc, c	2
	L, M			a_2	ab	3
12	MN, NL, N	A''		b_1	a, ac	2
				b_2	b, bc	2

^a The molecular axes (*L*, *M*, *N*) are shown in Fig. 1. *Z* is the number of fundamentals for the free molecule and *n* is the number of lattice frequencies. Crystal symmetry species are distinguished by the use of lower-case letters.

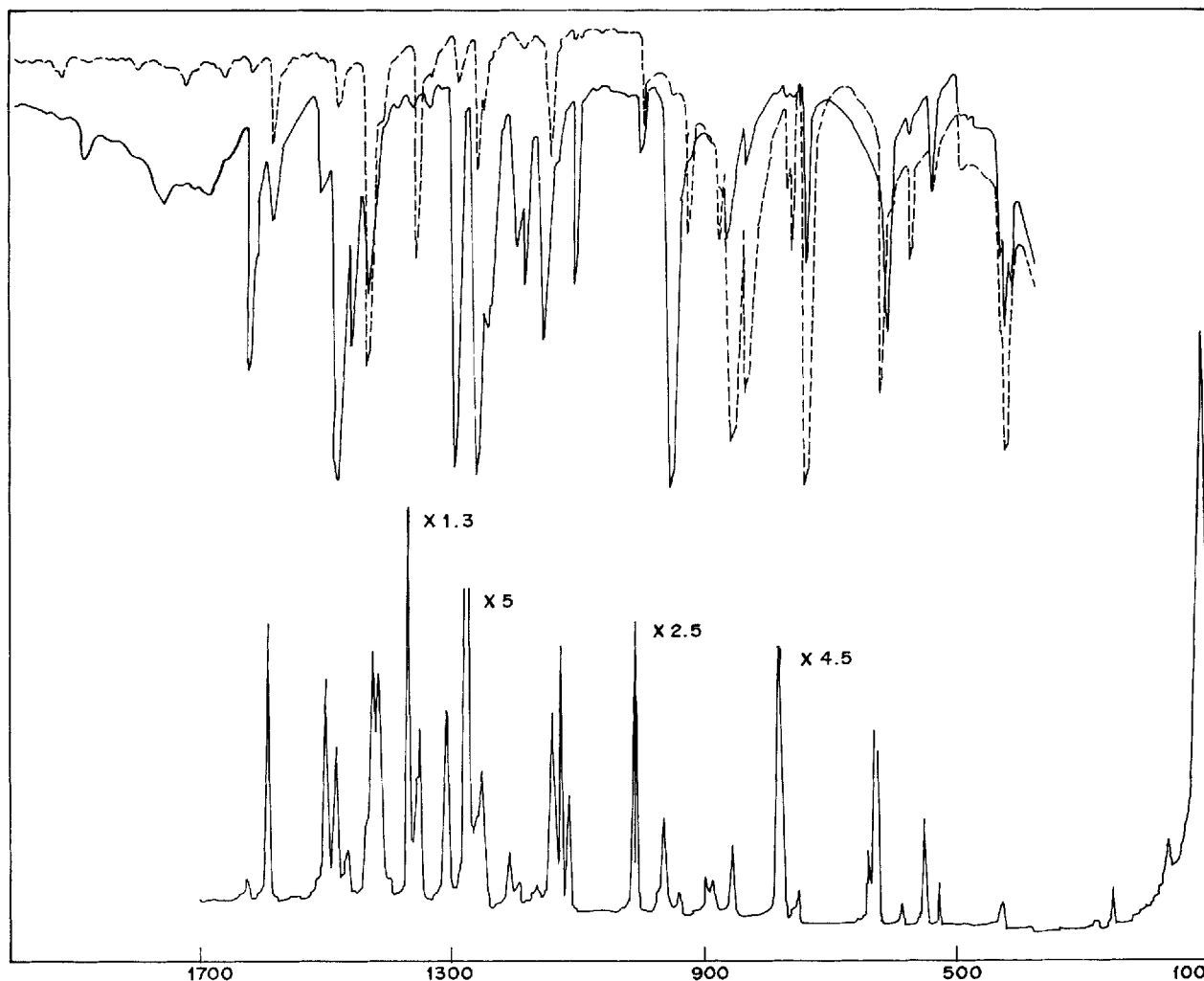


Figure 2. Top: IR spectra of crystalline benzimidazole. The full line is the spectrum parallel to the *b* axis of the crystal and the broken line that parallel to the *c* axis. Bottom: Raman spectrum of polycrystalline benzimidazole.

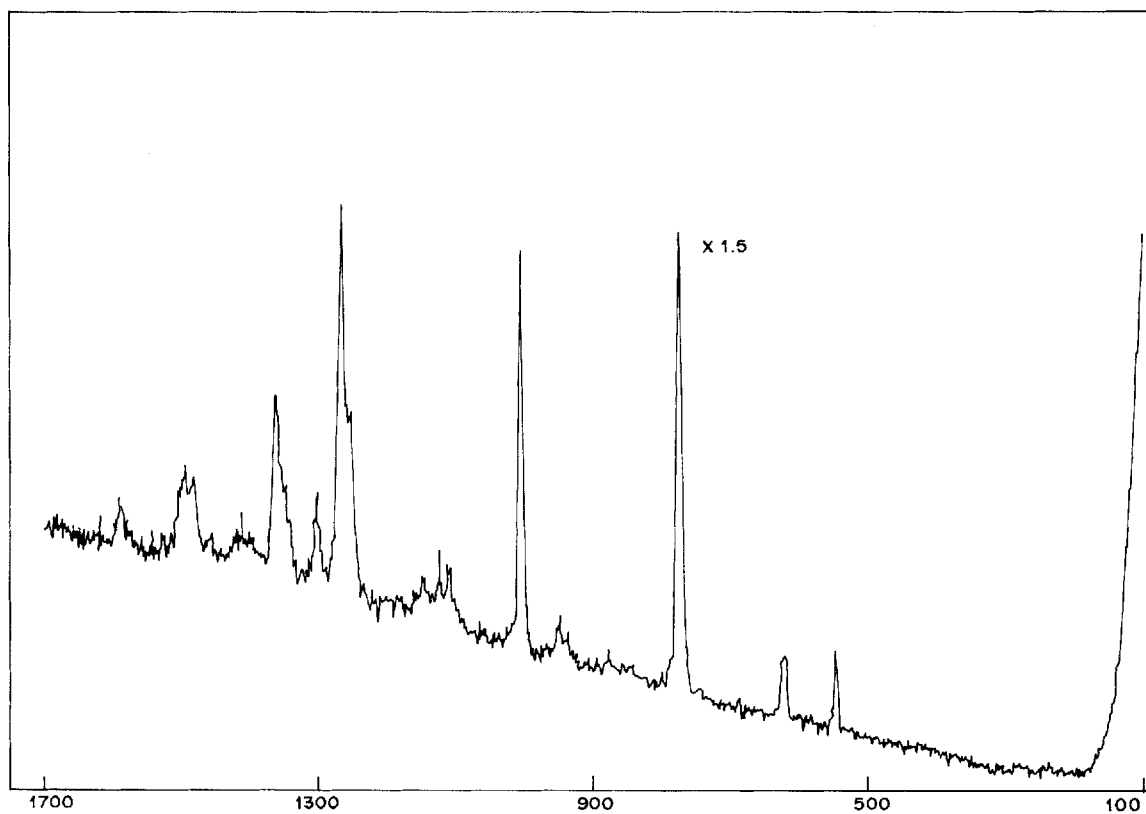


Figure 3. Raman spectrum of benzimidazole melt.

Table 3. Infrared and Raman spectra of benzimidazole

IR ³ KBr disc	Solid	IR ⁸ Soln	Raman ⁸ Solid	Abs. ⁹ gas	Phos. ¹⁰ mix Xl	IR ² KBr mull	Assignments ³	IR ^a Solid		Melt	Raman ^a r	Crystal	Assignments ^a	Raman ¹¹	Int.	Fluor. ¹¹	Int.	
	3110 s	3333 w, br				3115 3097 3065 3040 3005 (b) 2968 (b) 2940 (b) 2890 (b) 2860 (b) 2790 (b) 2620 2540 1932 1897 1815 1770 w 1620 w 1600 w	CH stretch NH stretch 1007 + 935 Overtone Overtone Ring stretch											
	3060 s																	
	2800 s, br																	

1138 m	1135 s	1138 m	1138 s	NH in-plane bend	1138 m	1126	0.57	1139 m	A', f	1138	39	1138	35
1005 m	1004 s	1110 w	1117	BZ in-plane CH bend	1115 w	1116	0.32	1125 m	A', f				
960 m	958 m	1006 s	1010	Bz in-plane bend	1006 m	1009	0.02	1008 s	A', f	1004	37	1003	34
	933 w	936 vw	1007 s	Im in-plane bend	950 vs	b		962 vw	A', f	963	1	963	2
890 m	897 vw	892 vw	940 w	Bz in-plane bend	929 m	b	0.63	936 vw	A"				
	888 s	884 vw	890 s	Im in-plane bend	890 vw			892 w	A"				
	882 sh				880 m			884 w	A"				
	847 vw	820 vw, br	848 m	Im CH out plane bend	848 s			851 w	A"	850	3	849	3
	778 sh	779 vs	775 s		837 s	778	p	780 vs	A', f	777	82	777	86
770 m	773 w	774 sh		In-plane ring bend	772 w								
748 s	769 s	770 m	771	Bz CH out-of-plane bend	760 m			752 vw	A", f				
	752 s	750 s	776	Bz out-of-plane bend	740 vs			748 w	A", f				
	745 s	660 w, br											
	634 m	636 w	626	In ring torsion	637 m			637 w	A', f				
	626 m	627 m		NH out-of-plane bend	628 m	628	dp	628 w	A", f				
	616 w	619 m	619 m	In-plane ring bend	619 m	b	0.74	620 w	A', f	617	26	617	16
	577 w	600 w, br			578 w			581 vw	A", f				
	540 w	570 w	548	Ring torsion	544 w	b	0.11	547 w	A', f	542	5	542	7
			421	Ring torsion	424 m			422 w	A", f	417	1	419	1
					419 m	b		269 vw	A", f				
				Lattice	274			246 w	A', f				
					242								
					272 m			157 w					
					244 m			114					
					228 m			108					
					157 m			93					
					108 m			88					
								81		81	4		
								77					
								66					
								55					
								47					
								42		41	2		

^a This work.

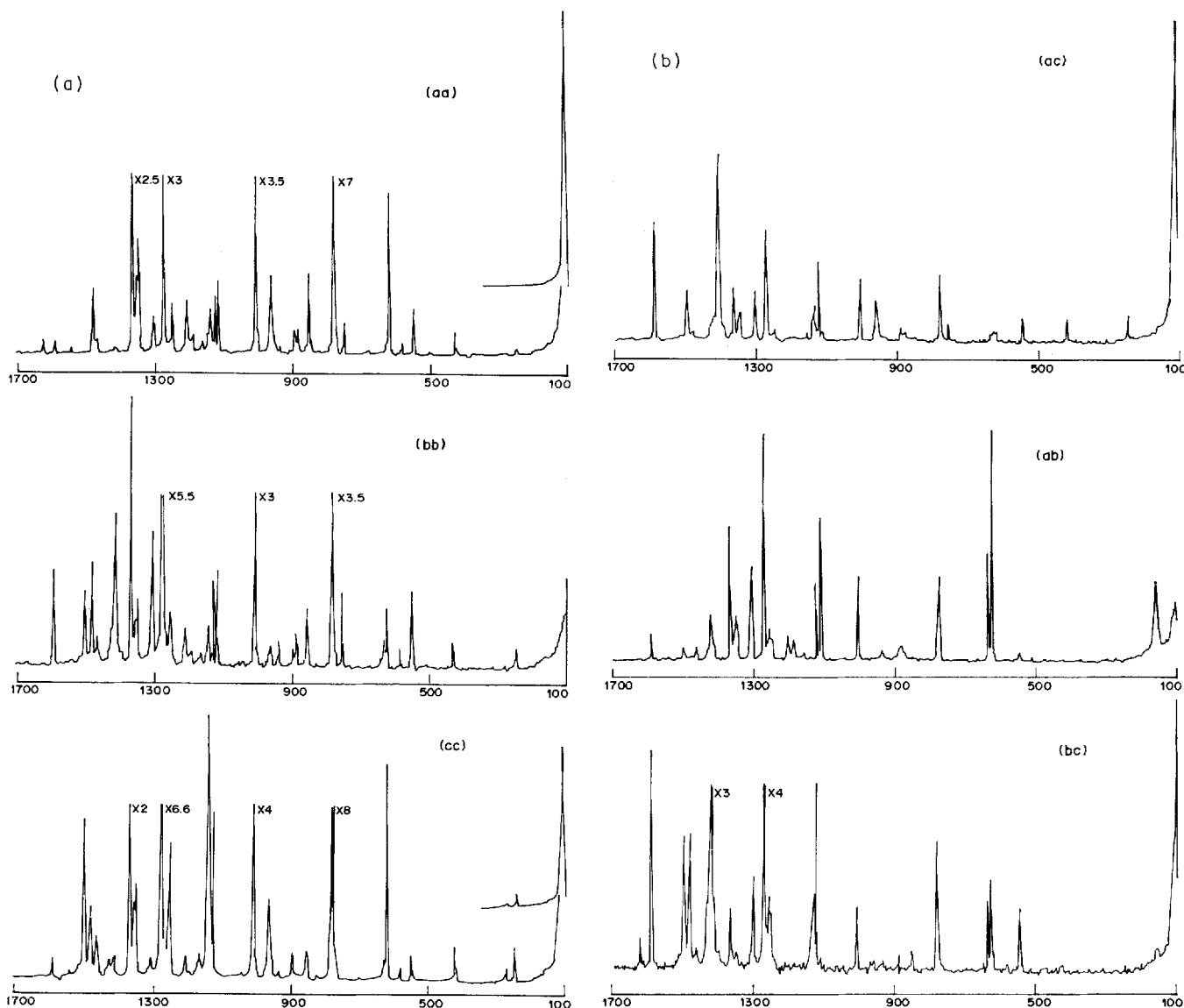


Figure 4. (a) Representative Raman spectra from a single crystal of benzimidazole grown by the Bridgman method. Indicated inside parentheses from left to right are the polarization of the incident light and scattered light, respectively. (b). Polarized Raman spectra of benzimidazole.

bands at 1485 and 1460 cm^{-1} . The 544 and 619 cm^{-1} bands may correlate with the 606 cm^{-1} (e_{2g}) benzene band.

Deuteration at the 1- and 2-positions on the imidazole rings has been used to distinguish between the bending modes of the hydrogens of the imidazole ring. On deuteration at these two positions, bands² at 1589 and 1138 cm^{-1} disappeared, indicating that they can be assigned to NH in-plane bending of the imidazole ring. Similarly, the 628 and 848 cm^{-1} vibrations are assigned to the NH and CH out-of-plane modes, respectively.

The observed bands in the Raman spectrum of the single crystal at 111 and 157 cm^{-1} have also been observed in the imidazole spectrum¹² and have been assigned to lattice vibrations involving the hydrogen bond.

The nature of the hydrogen bond between benzimidazole molecules as revealed by its influence on the N—H stretching modes has been thoroughly investigated.^{3,13,14} In dilute solutions, the IR absorption occurs at 3400 cm^{-1} whereas in concentrated solutions a broad absorption band at about 3200 cm^{-1} is

observed. In contrast to the N—H $\cdots\pi$ type of hydrogen bonding that has been suggested for indole¹ and pyrrole,¹⁵ benzimidazole has the N—H \cdots N type of hydrogen bonding where the distance between the hydrogen of one molecule and the nitrogen of the neighbouring molecule is 2.00 Å, indicating that the effect of the hydrogen bond on the benzimidazole spectra will be greater. The IR band at 628 cm^{-1} is shifted to 544 cm^{-1} on deuteration, indicating that this mode is coupled to the γ NH motion. Its breadth can be attributed to the influence of the hydrogen bonding. Also, on deuteration the band at 1138 cm^{-1} disappears and a new band at 987 cm^{-1} appears. This band has been assigned to NH in-plane bending mode.

Acknowledgements

We are grateful to Prof. A. Bree for providing us with his electronic spectroscopy analysis of benzimidazole electronic spectroscopy prior to its publication. Support from the King Fahd University of Petroleum and Minerals is gratefully acknowledged.

REFERENCES

1. A. Suwaiyan and R. Zwarich, *Spectrochim. Acta, Part A* **42**, 1017 (1986).
2. M. M. Cordes and J. L. Walter, *Spectrochim. Acta, Part A* **24**, 1421 (1968).
3. H. G. Tompkins, D. L. Allara and G. A. Pasteur, *Surf. Interface Anal.* **5**, 101 (1983).
4. P. Bassignana, C. Cogrossi, M. Gandino and P. Merli, *Spectrochim. Acta* **21**, 605 (1965).
5. Par A. Escande and J. L. Galigne, *Acta Crystallogr., Sect. B* **30**, 1647 (1974).
6. C. J. Dik-Edixhoven, H. Schent and H. van der Meer, *Cryst. Struct. Commun.* **2**, 23 (1973).
7. A. N. Winchell, *The Optical Properties of Organic Compounds*, p. 205. Academic Press, New York (1954).
8. B. Borah and J. L. Wood, *Can. J. Chem.* **54**, 2470 (1976).
9. R. D. Gordon and R. F. Yang, *Can. J. Chem.* **48**, 1722 (1970).
10. M. Noda, S. Nagaoka and N. Hirota, *Bull. Chem. Soc. Jpn.* **57**, 2376 (1984).
11. A. Bree, personal communication.
12. M. M. Cordes and J. L. Walter, *Spectrochim. Acta, Part A* **24**, 237 (1968).
13. K. Pragerova and V. Bekarek, *Acta Univ. Palack. Olomuc Fac. Rerum Nat.* **53**, 71 (1977).
14. H. Fritzsche, *Spectrochim. Acta* **22**, 1139 (1966).
15. M. Campos-Vallete, K. A. Figueroa and V. Vargas, *Spectrochim. Acta, Part A* **44**, 601 (1988).