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Adriano Bigotto^a; Achyuta Nand Pandey^a; Carmelo Zerbo^a

^a Department of Chemical Sciences, University of Trieste, Trieste, Italy

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**POLARIZED INFRARED AND RAMAN SPECTRA AND
Ab-Initio CALCULATIONS OF BENZOTRIAZOLE**

Key words: benzotriazole, infrared, Raman, polarized spectra,
Ab-Initio Calculations

Adriano Bigotto*, Achyuta Nand Pandey[§] and Carmelo Zerbo

Department of Chemical Sciences, University of Trieste
Via L.Giorgieri 1, 34127 Trieste, Italy

ABSTRACT

The i.r. spectra of benzotriazole have been measured from 4000 to 60 cm⁻¹; polarized spectra of single crystals have been also obtained. The Raman spectra of polycrystalline samples and solutions have been investigated. The structural parameters and vibrational frequencies have been determined from *ab-initio* Hartree-Fock gradient calculations using the 6-31G* basis set. A detailed assignment of most of the observed bands has been proposed on the basis of the i.r. dichroism, Raman polarization data and frequency calculations.

INTRODUCTION

Benzotriazole and its derivatives show significant biological activity and have important applications as dyestuffs, optical brighteners and photostabilizers: moreover, they act as powerful corrosion inhibitors for many metals and alloys¹. In connection to this latter property, much attention has been devoted to the elucidation of the inhibition mechanism. To this purpose, vibrational spectroscopic methods such as SERS⁵⁻¹⁵ and IRRAS¹⁶⁻²³ play an important role in clarifying the interaction

* Author to whom correspondence should be addressed

§ Present address: Department of Physics, Meerut College, Meerut, India.

mechanism between the adsorbed molecules and the metal surfaces. For a correct interpretation of the spectral data, all these techniques require detailed and well established assignments for the vibrational modes of interacting molecules. At our best knowledge, the available assignments of benzotriazole²⁻⁵ have been proposed mainly on correlative grounds, although a vibrational analysis has been also carried out⁴ and some vibrational modes involving the NH group have been assigned with the aid of the deuteration methods⁵. In order to put the assignments on a more firm basis an investigation of the polarized i.r. spectra of single crystals has been undertaken and the i.r. and Raman spectra of polycrystalline solids and solutions have been reinvestigated. The experimental spectra have been compared with the results of an *ab-initio* calculation for the harmonic frequencies. Vibrational assignments have been proposed on the basis of the of the i.r. dichroic data and of the polarization of the Raman bands, keeping in mind the results of the theoretical calculations.

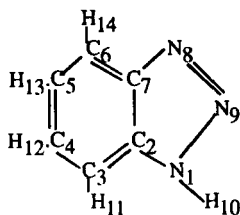
EXPERIMENTAL

Benzotriazole *puriss.p.a.* from Fluka was used without further treatments. Single crystals, in the form of thin sheets, were obtained by slow evaporation of benzene solutions. X-ray methods showed that the well developed plane of the crystals used in absorption measurements contained the **b** and **c** axes. The i.r. spectra were recorded on Perkin-Elmer 983G and System 2000 spectrophotometers. Polycrystalline samples were in the form of KBr pellets and Nujol mulls. Carbon tetrachloride, chloroform and carbon disulphide were used to obtain i.r. spectra of solutions. The measurements of the polarized spectra were carried out using a wire-grid polarizer and a beam-condenser. Low temperature spectra were obtained using a Beckmann-RIIC VLT2 unit. The Raman spectra were obtained with a SPEX Ramalog spectrometer using the 488.0 nm line of a Spectra-Physics model 165 Ar⁺ laser for the excitation. The samples were enclosed in capillary cells. Depolarization ratios were measured for methanol solutions.

Details of calculations

The geometry of benzotriazole was optimized within the Hartree-Fock method using the 6-31G* basis, without any assumption about the planarity of the molecule. The atom numbering is indicated in Scheme 1. The harmonic frequencies and the normal modes were calculated analitically at the same level of approximation using the following optimized parameters obtained from the previous step (distances in Å, angles in degrees): N₁C₂=1.3548; C₂C₃=1.4002; C₃C₄=1.3699; C₄C₅=1.4144; C₅C₆=1.3689; C₆C₇=1.3998; N₈C₇=1.3746; N₈N₉=1.2529; C₃H₁₁=1.0743; C₄H₁₂=1.0752; C₅H₁₃=1.0746; C₆H₁₄=1.0739; N₁C₂C₃=134.7507; C₂C₃C₄=116.1053; C₃C₄C₅=122.1575; C₄C₅C₆=121.2042; C₅C₆C₇=117.2401; C₆C₇N₈=130.8586; C₇N₈N₉=108.5712; N₉N₁H₁₀=119.0515; C₄C₃H₁₁=121.6978; C₃C₄H₁₂= 119.1702; C₄C₅H₁₃= 118.8218; C₅C₆H₁₄= 122.0399; C₄C₃C₂N₁=180.0009; C₅C₄C₃C₂=0.0006; C₆C₅C₄C₃=-0.0004; C₇C₆C₅C₄=0.0001;

$N_8C_7C_6C_5=179.9977$; $N_9N_8C_7C_6=179.9935$; $H_{10}N_1N_9N_8=179.9923$;
 $H_{11}C_3C_4C_5=180.0004$; $H_{12}C_4C_3C_2=180.0001$; $H_{13}C_5C_4C_3=179.9996$;
 $H_{14}C_6C_5C_4=179.9995$.



Scheme 1.

All reported calculations were performed using the GAUSSIAN 92 program²⁴. The calculated wavenumbers were scaled down by a factor of 0.90 to account for the electronic correlation effects²⁵.

RESULTS AND DISCUSSION

Selection rules and spectral predictions

Crystals of benzotriazole are monoclinic, space group $P2_1$ (C_2^2)²⁶. There are eight molecules in the unit cell, located on C_1 sites, which are distributed into four independent sets. The molecules are connected by a rather complicated system of hydrogen bonds. The selection rules for the benzotriazole molecules and the crystal are given in Table 1. Since both x-ray data and *ab-initio* calculations give a substantially planar structure, the C_s symmetry is assumed for the molecule.

TABLE 1

Selection rules for the free molecule and the unit cell of Benzotriazole

Molecule C_s	Site C_1	Unit cell C_2
A' 25 (i.r.,R)	A 36 (i.r.,R)	A 167 (23 L)+T _b (i.r.,R)
A'' 11 (i.r.,R)		B 166 (22 L)+T _{ac} (i.r.,R)

L=Lattice modes

According to the above Table, each molecular fundamental should give two components in the crystal spectrum, active both in Raman and i.r., one being polarized along the **b** axis, the other in the **ac** plane. The A' and A'' molecular fundamentals could be discriminated, to some extent, on the basis of the Raman polarization data of the solutions.

Informations concerning the assignments of the i.r. bands can also be obtained from the consideration of their dichroism. The oriented gas model may be used to predict the behaviour in polarized light. For the isolated molecule, only the direction of the transition moments of the A'' vibrations is fixed by symmetry and using the atomic coordinates given by Escande *et al.*²⁶ the proportionality factors for the absorption intensities are

		$a^*(\perp bc)$	b	c
Set 1	$I(A'')$	0.016	0.287	0.679
Set 2	$I(A'')$	0.022	0.196	0.782
Set 3	$I(A'')$	0.062	0.172	0.766
Set 4	$I(A'')$	0.020	0.310	0.670

From these values it can be argued that, in the polarized i.r. spectra of the **bc** crystal plane, the A'' out-of-plane modes should give the strongest component when the electric vector of the light is perpendicular to the **b** crystal axis. Bands showing a strong component parallel to the **b** axis or components of nearly equal intensity in both polarizations can be confidently assigned to A' in-plane modes.

Vibrational assignments

The polarized i.r. spectra are shown in Figure 1 and the relevant i.r. and Raman data are collected in Table 2 together with the assignments. The approximate descriptions of the fundamentals are given with reference to the normal modes obtained from the *ab-initio* calculation.

The hydrogen bonding strongly affects the position and shape of the bands associated to the NH stretching mode. This fundamental is observed as a sharp i.r. band at 3463 cm^{-1} for the free molecule in CCl_4 solutions, whereas in the solid state it is associated to the very broad absorption ranging from 3400 to 2100 cm^{-1} . This absorption, whose center of gravity moves to 2370 cm^{-1} upon deuteration and undergoes a red shift of approximately 10 cm^{-1} on cooling to -140°C , is highly structured, with several submaxima which show the same polarization in the single crystal spectra. This observation rules-out the possibility that they are due to correlation field splitting. As for the parent compound 1,2,4-triazole²⁷ the NH band structure can be accounted for in terms of combinations and overtones gaining intensity through Fermi resonance (F.R.) with the NH stretching fundamental. In the present case the

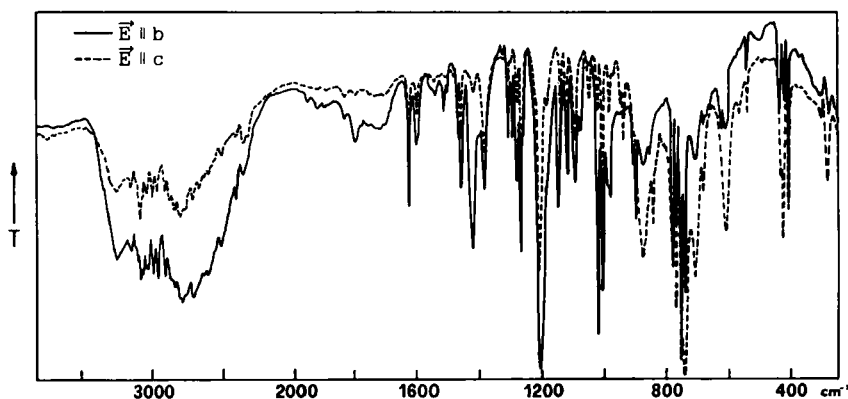


Fig. 1. Polarized i.r. spectra of benzotriazole, bc crystal plane

resonance interaction is favoured by the presence of a multiplicity of hydrogen-bonds of different strength in the solid state, which give rise to different NH-bonded stretching frequencies. In fact, there are two N...N distances of 2.81 and 2.83 Å, which correspond to short hydrogen-bonds with small deviation from linearity, and four N...N distances ranging from 3.09 to 3.14 Å, which correspond to longer and likely bifurcated hydrogen-bonds. According to the correlation diagrams reported by Novak²⁸ the NH stretching frequencies for the group of short NH...N bonds are predicted in the range 2650-2700 cm⁻¹, whereas for the group of long NH...N bonds the stretching frequencies should occur in the range 3200-3300 cm⁻¹. Fundamentals in the 1650-1100 cm⁻¹ region can give several combinations and overtones with frequencies falling near the above values.

Some features of the absorption spectra in the region below 1000 cm⁻¹, related to the γ NH₂ mode can also be accounted for in terms of the multiplicity of the NH...N bonds. Three bands are observed at 879, 710 and 608 cm⁻¹, which disappear on deuteration and clearly show the polarization parallel to the c axis predicted for the out-of-plane vibrations: moreover, upon cooling to -140°C, the absorption maxima move to 894, 716 and 617 cm⁻¹, respectively, with a simultaneous reduction of the half-bandwidth and an increase of the maximum intensity. In the light of the above observations they can be attributed to out-of-plane modes of NH groups involved in NH...N bonds of increasing length and decreasing strength. The present assignment differs from that proposed by Rubim *et al.*⁵, who assigned the bands at 710 and 608 cm⁻¹ to a combination tone and to a ring torsion, respectively. The corresponding mode of the "free" molecule can be associated to the band observed at 494 cm⁻¹ both

TABLE 2

Experimental spectral data, calculated frequencies(scaled values) and assignments for Benzotriazole

i.r frequencies and polarizations(P)			Raman shift and polarization		Calc.	Assignments
solid	P	solution	solid	solution		
		3463 m			3534	A'v ₁ v NH
3351 mb	b>c					
3251 mb	b>c					
3147 m	b>c				}	v NH(..N)+ F.R.
3115 m	b>c		3122 vw			
3100 m	b>c		3100 vw			
3080 w	b>c	3079 w	3077 ms	3080 m,p	3062	A'v ₂ v CH
3077 sh	b>c		3069 m		3053	A'v ₃ v CH
3050 w	b>c	3059 w	3065 m		3042	A'v ₄ v CH
			3052 vw			
3031 w	b>c	3040 w	3034 vw		3029	A'v ₅ v CH
2993 m	b>c					
2960 m	b>c					
2911 m	b>c					
2875 mw	b>c					
2841 m	b>c					
2795 ms	b>c					
2765 m	b>c					
2745 sh	b>c				}	v NH(..N)+ F.R.
2713 m	b>c					
2675 mw	b>c					
2640 mw	b>c					
2610 mw	b>c					
2562 w	b>c					
2520 w	b>c					
2412 w	b>c					
....			
1623 m	b>c	1622 m	1625 w	1628 w,dp	1646	A'v ₆ v skeletal
1596 w	b>c	1594 m	1596 ms	1598 w,p	1616	A'v ₇ v skeletal
1539 vw	b>c				A' 2v ₂₉	
1513 w	b>c		1515 w	1512 w,p	1518	A'v ₈ v skeletal
1498 w	b>c	1492 m	1501 w		A' v ₁₈ + v ₂₅	
1470 sh	b>c		1472 w		A' 2v ₃₀	
1463 m	b>c	1453 m	1458 w	1468 w,p	1490	A'v ₉ v skeletal

TABLE 2 (cont.)

i.r frequencies and polarizations(P)			Raman shift and polarization		Calc.	Assignments
solid	P	solution	solid	solution		
1421 m	b		1422 vw		1436	A'v ₁₀ v skeletal + δ CH
1384 m	b>c	1382 m	1389 vs	1388 vs,p	1398	A'v ₁₁ v skeletal + δ NH + δ CH
			1374 m	1373 m,p		A' 2v ₁₉ FR with v ₁₁
1310 w	b>c		1311 w			A' v ₂₂ + v ₂₄
1300 w	b	1298 mw	1299 w	1308 w,p	1290	A'v ₁₂ v skeletal + δ CH
1281 m	b>c		1283 m	1281 mw,p	1285	A'v ₁₃ v skeletal + δ NH + δ CH
1269 m	b>c	1260 mw	1272 w		1255	A'v ₁₄ v skeletal + δ CH + δ NH
1263 sh	b=c					A' 2v ₂₃
1210 vs	b>c	1213 ms	1212 m	1220 w,p	1218	A'v ₁₅ v skeletal + δ CH
1185 sh	b>c					A' v ₂₂ + v ₂₅
1148 mw	b					
		} 1143 mw	1151 w	1151 w,p	1123	A'v ₁₆ δ CH
1140 w	c					
1124 w	c		1131 m			
		} 1123 mw		} 1131 w,dp	1107	A'v ₁₇ δ CH
1119 w	b		1119 w			
1095 m	b>c		1100 m			
		} 1083 mw		} 1092 mb,p	1070	A'v ₁₈ δ NH
1079 m	b		1080 w			
1040 w	c		1048 w			? v ₂₃ + v ₂₅
1024 m	b>c	1017 sh	1025 ms		1000	A'v ₁₉ δ CH + δ skeletal
1015 mw						
1008 m	b>c	1008 m	1010 m	1014 s,p	977	A'v ₂₀ δ skeletal + δ CH
992 sh	b	993 w	996 w			A' v ₃₂ + v ₃₄
982 w	b>c					A' v ₃₀ + v ₃₆
(972 vw)*	c	960 w			1005	A''v ₂₆ γ CH?
949 w	c	940 w	945 vw	950 vw,?	973	A''v ₂₇ γ CH
938 w	c					? v ₂₄ + v ₂₅
909 mw	b=c					
		} 902 w	906 w	908 w,p	882	A'v ₂₁ δ skeletal + δ CH
900 mw	b					
879 mb	c>b		871 vw			γ NH(..N)
845 w	c	843 w	850 vw	858 vw,dp	866	A''v ₂₈ γ CH + τ skeletal

(continued)

TABLE 2 (cont.)

i.r frequencies and polarizations(P)			Raman shift and polarization		Calc.	Assignments
solid	P	solution	solid	solution		
780 m	b=c	778 m	783 vs	782 vs,p	763 A''v ₂₂	δ skeletal
771 mw	c>b	768 sh	770 sh		774 A''v ₂₉	γ CH + τ skeletal
753 m	b=c					
742 vs	c>b	744 vs	751 vw		759 A''v ₃₀	γ CH
709 mb	c>b					γ NH(..N)
(677 vw)*	c>b	682 m			693 A''v ₃₁	τ skeletal + γ CH
633 w	b=c	626 w	633 m	633 m,dp	618 A''v ₂₃	δ skeletal
610 mw	b>c					γ NH(..N)
569 vw	c	573 m	570 vw	572 vw,dp	573 A''v ₃₂	τ skeletal + γ CH
539 w	b=c		540 m	542 m,p	524 A''v ₂₄	δ skeletal
		494 msb			450 A''v ₃₃	γ NH
433 sh	c>b					
427 m	c>b	428 ms	434 vw	437 vw,?	430 A''v ₃₄	τ skeletal
408 m	b>c	412 m	408 vw	419 vw,?	400 A''v ₂₅	δ skeletal
286 m	c>b	270 mw	279 vw	278 vw,dp	261 A''v ₃₅	τ skeletal
279 sh						
239 mw		238 vw	239 w	232 vw,dp	218 A''v ₃₆	τ skeletal
			224 sh			
138 mw						lattice
121 m			119 sh			lattice
107 sh			109 vs			lattice
			98 vs			lattice
93 w						lattice
			83 vs			lattice
77 mw						lattice
			70 m			lattice
64 w						lattice
			53 s			lattice
			41 m			lattice
			29 m			lattice

* observed in the single crystal spectrum

b: bands polarized parallel to the **b** crystal axis;

c: bands polarized parallel to the **c** crystal axis

s=strong,m=medium,w=weak,b=broad; p=polarized, dp=depolarized

v=stretching, δ =in-plane bending, γ =out-of-plane bending, τ =torsion

in CCl_4 and CS_2 solutions. This value compares satisfactorily with the calculated value of 450 cm^{-1} for the normal mode possessing the strongest contribution of the out-of-plane motion of the NH group.

The available data don't allow an unambiguous attribution of the in-plane NH bending mode. Deuteration affects the position and intensity of several bands between 1650 and 1000 cm^{-1} , revealing a contribution from the NH bending coordinate to the fundamentals in this range. However, variable temperature measurements show that the bands at 1080 and 1095 cm^{-1} undergo the most remarkable blue-shift on cooling to -140°C (6 cm^{-1}) suggesting that these absorptions are the most probable candidates for this assignment, in agreement with the proposal of Rubim *et al.*⁵ who assigned a band at 1092 cm^{-1} to this fundamental. The calculations confirm that the in plane bending of the NH group remarkably contributes to the character of the normal mode calculated at 1070 cm^{-1} , but sizeable contributions are also found for several other modes.

The structure of the NH absorption makes uncertain the assignment of the CH stretching modes in the i.r. spectra. The assignment is easier for the Raman spectra, where the intensity of the NH stretching band is very low. Three of the corresponding fundamentals for the benzene ring can be assigned to the Raman bands at 3077 , 3069 , and 3031 cm^{-1} . There are two candidates for the fourth mode, namely the bands at 3065 cm^{-1} and 3059 cm^{-1} : the present choice of the former band is tentative and mainly suggested by the intensity.

As to the remaining fundamentals, Raman polarization data suggest the assignment to A' modes of the polarized bands observed at 1598 , 1512 , 1468 , 1388 , 1308 , 1281 , 1220 , 1151 , 1014 , 908 , 782 and 542 cm^{-1} . Another A' fundamental may be associated to the depolarized Raman band at 633 cm^{-1} on the basis of the observation that the corresponding infrared absorption shows crystal components of comparable intensity both in the polarization parallel and perpendicular to the **b** axis. Likewise, the Raman band at 1628 cm^{-1} , assigned to the ν_6 skeletal stretching mode, is also depolarized, but the corresponding infrared absorption shows a prevailing polarization parallel to the **b** axis. The attribution of ν_{25} to the i.r. band at 408 cm^{-1} is also suggested by the dichroism.

Three γCH fundamentals are assigned to the absorption bands observed at 744 , 843 and 940 cm^{-1} in solution, on the basis of the prevailing polarization perpendicular to the **b** axis shown by their counterparts in the single crystal spectra. As to the remaining γCH fundamental, no obvious candidate can be proposed. The band observed at 1040 cm^{-1} shows the correct polarization along the **c**-axis: however, it lies out of the generally accepted range for this mode, since correlative arguments based on the assignments for o-disubstituted benzenes²⁹ suggest that it should be located near 970 cm^{-1} . The choice of the very weak band at 972 cm^{-1} , which is observed only in the single crystal spectra in the polarization perpendicular to the **b** axis, must be considered as tentative.

Lastly, three of the remaining A'' fundamentals may be assigned to the depolarized Raman bands at 572 , 278 and 232 cm^{-1} . The assignment of the first two modes is

further supported by the polarization parallel to the *c* axis shown by their i.r. counterparts. The polarization parallel to the *c* axis also suggests the choice of the i.r. band at 427 cm⁻¹ as a fundamental of A" species.

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