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# Vibrational Assignments and Analysis for 2-Benzimidazole Thione

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The Laser Raman and FTIR spectra of 2-benzimidazole thione have been recorded in the region 4000–100 $cm^{-1}$. The observed frequencies were assigned to different modes of vibrations on the basis of fundamental, combination and overtones and normal coordinate analysis assuming $C_S$ point group symmetry. The potential energy distributions (PEDs) associated with each vibrational type is also reported. Further, based on the present assignments, a complete vibrational analysis was carried out for this compound. The results are briefly discussed.

## INTRODUCTION

Benzimidazoles are known for their commercial and biological importance as pharmaceuticals, veterinary anthelmintics and fungicides. In particular, benzimidazole-2-thione is effective in preventing the dissolution of carbon-steel in acidic media[1] and corrosion of brass and aluminium in alkaline solutions[2, 3]. Thus, a vibrational study of the benzimidazole-2-thione molecule can provide information about their coordinate mechanism at the metal surface. The vibrational spectra of thiazoles and benzothiazoles have already been reported[4–8]. In the present investigation, we report the complete vibrational analysis of benzimidazole-2-thione bases on the FTIR and Raman spectra of the compound and assigned the frequencies to the various modes of vibrations using the fundamentals, combination and overtones and normal coordinate calculations. The structural parameters used for the calculation are taken from similar compounds[9, 10].

## EXPERIMENTAL

The pure 2-benzimidazole thione was obtained from Fluka Chemical A.G., Switzerland and used as such. The FTIR spectrum of 2-benzimidazole thione in KBr disc was recorded on a Nicolet 20 DXB spectrometer in the region 4000–400 $cm^{-1}$ at C.L.R.I., Madras. The laser Raman spectrum was also recorded in the region 4000–200 $cm^{-1}$ on a Cary Model 82 grating spectrophotometer operating at 4 W power, at a scanning speed of 30 $cm^{-1}$ $min^{-1}$, and a spectral width of 2 $cm^{-1}$. These spectra are shown in figures 1 and 2. The frequencies for all sharp bands are accurate to ±1 $cm^{-1}$.

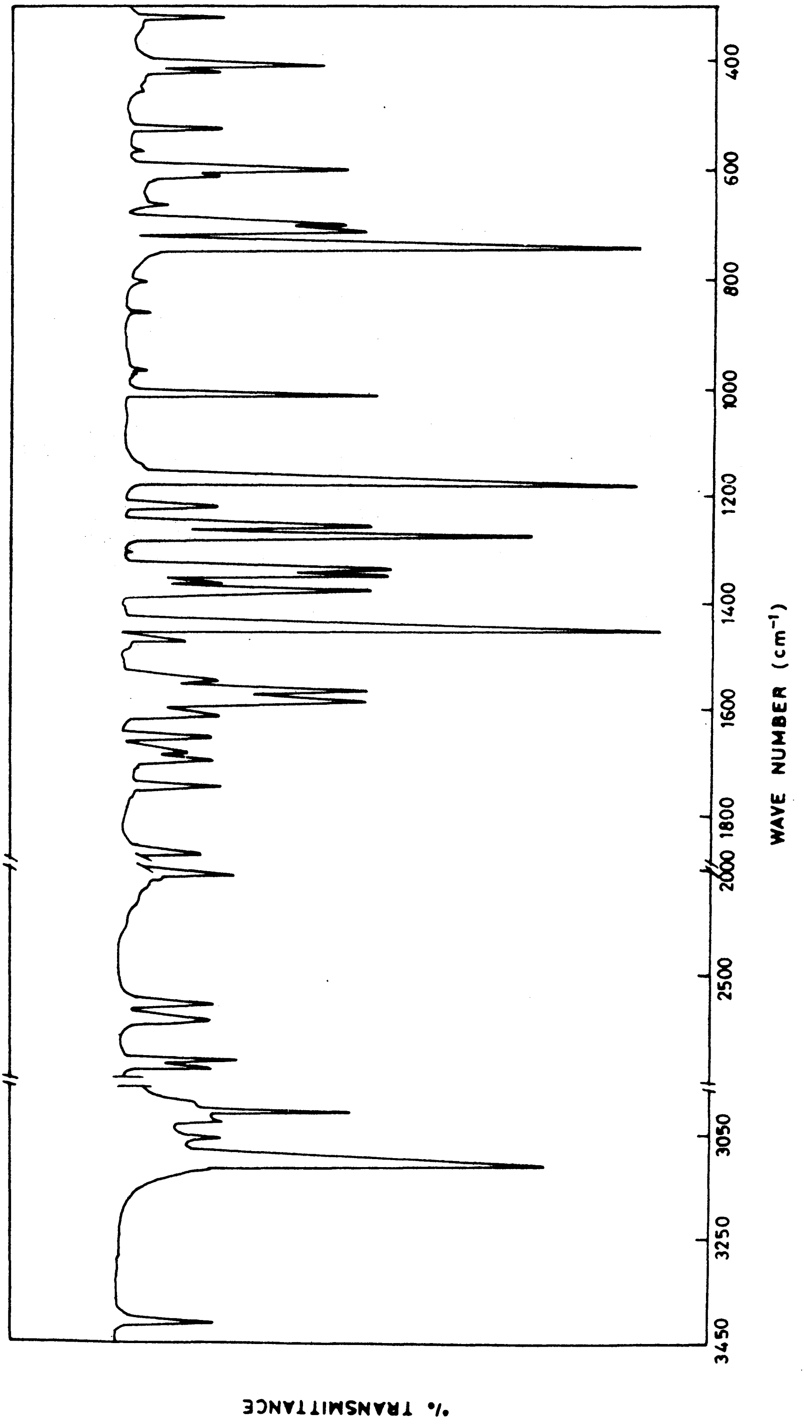

Fig. 1. FTIR Spectrum of benzimidazole-2-thione

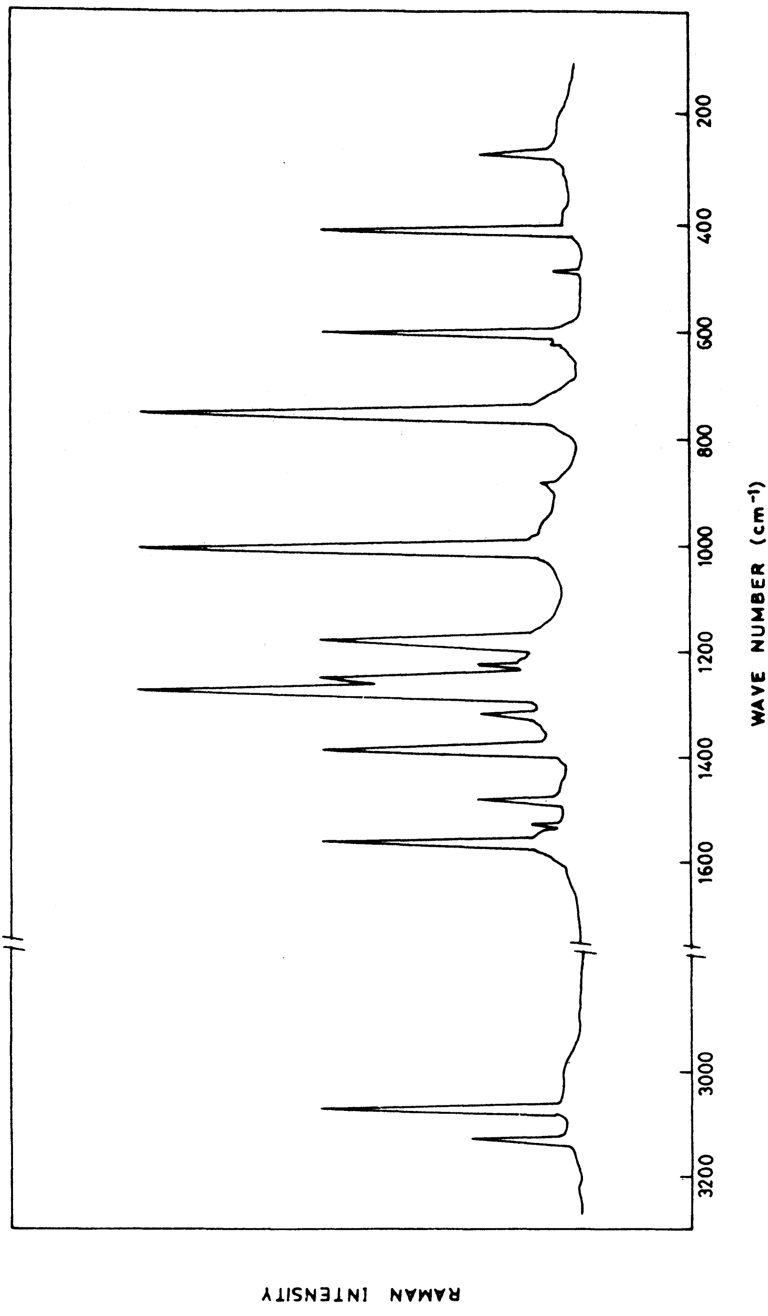

Fig. 2. Laser raman spectrum of benzimidazole-2-thione

## Normal Coordinate Analysis

The observed frequencies with their relative intensities and probable assignments are presented in Table-1 along with the calculated frequencies. The molecule benzimidazole-2-thione belongs to $C_S$ symmetry and the 42 fundamental vibrational frequencies which are active in both IR and Raman, are distributed as

$$\Gamma_{vib} = 29a' \text{ (in-plane)} + 13a'' \text{ (out-of-plane)}$$

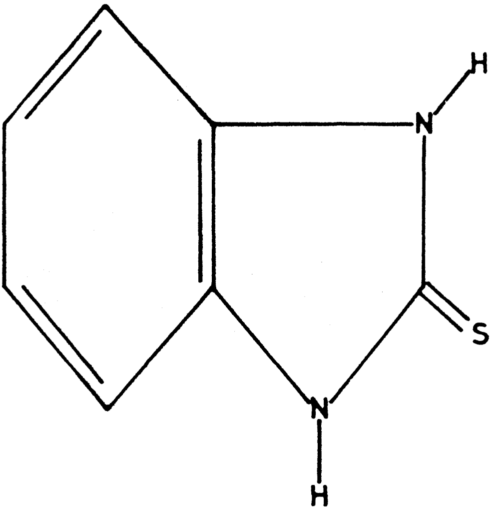

Fig. 3. Structure of Benzimidazole-2-thione

Wilson's F-G matrix method was used for the normal coordinate analysis. All the vibrations are both infrared and Raman active. The normal coordinate calculations were performed using the program developed by Mink *et al.*[12]. Internal coordinates for the out-of-plane torsional vibrations are defined as recommended by IUPAC. The general quadratic valence force field is adopted for both in-plane and out-of-plane vibrations.

The results of the normal coordinate calculation of the compound is also given in Table-1. The general agreement between the calculatled ad observed frequencies for both in-plane ad out-of-plane modes are good.

TABLE-1
OBSERVED AND CALCULATED FREQUENCIES AND POTENTIAL ENERGY DISTRIBUTION FOR BENZIMIDAZOLE-2-THIONE

| Species | IR $cm^{-1}$ | Raman $cm^{-1}$ | Cal. $cm^{-1}$ | Assignment | PED % |
|---|---|---|---|---|---|
| a′ | 3117 w | | 3415 | ν(N—H) | 98 |
| a′ | 3110 s | 3129 w | 3135 | ν(N—H) | 90 |
| a′ | 3060 w | 3072 m | 3067 | ν(C—H) | 97 |

| Species | IR cm$^{-1}$ | Raman cm$^{-1}$ | Cal. cm$^{-1}$ | Assignment | PED % |
|---|---|---|---|---|---|
| a′ | 3039 w | | 3045 | ν(C—H) | 95 |
| a′ | 3028 m | | 3038 | ν(C—H) | 94 |
| a′ | 3004 w | | 3005 | ν(C—H) | 96 |
| | 2960 w | | 2960 | 1574 + 1380 | |
| | 2725 w | | 2716 | 1380 + 1340 | |
| a′ | 1699 vw | | 1688 | ν(C—N) | 89 |
| a′ | 1659 w | | 1652 | ν(C—N) | 91 |
| a′ | 1618 w | | 1614 | ν(C—C) | 89 |
| a′ | 1595 m | | 1588 | ν(C—C) | 87 |
| a′ | 1574 m | 1565 m | 1571 | ν(C—C) | 93 |
| a′ | 1559 w | 1538 vw | 1547 | β(N—H) | 82 |
| a′ | 1487 vw | 1480 w | 1481 | ν(C—C) | 90 |
| a′ | 1450 vs | | 1461 | ν(C—C) | 88 |
| a′ | 1380 m | 1390 m | 1382 | ν(C—C) | 90 |
| a′ | 1375 w | | 1368 | β(N—H) | 81 |
| a′ | 1365 m | | 1345 | ν(C=S) | 80 |
| a′ | 1358 m | | 1349 | ν(C—N) | 82 |
| a′ | 1341 m | 1317 w | 1345 | ν(C—N) | 85 |
| a′ | 1274 s | 1275 s | 1255 | β(C—H) | 71 |
| a′ | 1260 m | 1254 m | 1249 | β(C—H) | 78 |
| a′ | 1228 w | 1235 w | 1214 | β(C—H) | 65 |
| a′ | 1181 vs | 1187 m | 1178 | β(C—H) | 42 |
| a′ | 1017 m | 1003 s | 1020 | Ring trigonal bending | 89 |
| a″ | 975 vw | | 981 | δ(C—H) | 75 |
| a″ | 869 vw | 873 vw | 853 | δ(C—H) | 69 |
| a″ | 813 vw | | 811 | Ring breathing | 90 |
| a″ | 743 vs | 751 s | 738 | δ(C—H) | 79 |
| a″ | 713 m | | 709 | δ(C—H) | 80 |
| a″ | 705 m | | 700 | δ(N—H) | 69 |
| a″ | 660 vw | | 651 | δ(C—C—C) | 77 |
| a″ | 615 w | 623 vw | 609 | δ(N—H) | 72 |
| a′ | 601 m | 600 m | 585 | β(C—C—C) | 74 |
| a″ | 569 vw | | 558 | δ(C—C—C) | 80 |
| a′ | 526 w | | 510 | β(C=S) | 70 |
| a′ | 495 w | 492 vw | 481 | β(C—C—C) | 64 |
| a″ | 464 vw | | 454 | δ(C—C—C) | 82 |
| a″ | 438 vw | | 430 | δ(C—C—C) | 81 |
| a″ | 427 w | | 416 | δ(C=S) | 65 |
| a′ | 417 m | 415 m | 409 | β(C—C—C) | 71 |
| a″ | 321 w | | 306 | β(C—C—C) | 53 |
| a″ | | 247 w | 232 | δ(C—C—C) | 49 |

## RESULTS AND DISCUSSION

*Carbon Vibrations*: In benzene the bands between 1650 and 1400 $cm^{-1}$ are assigned to C—C stretching modes. In the present case, the bands observed at 1618, 1595, 1574, 1487 and 1450 $cm^{-1}$ are assigned to this mode. The C—C ring breathing mode and C—C—C trigonal bending are assigned to the bands at 1017 and 813 $cm^{-1}$ respectively. The above assignments agree well with Murray and Galloway[13] and Golse and Thio[14].

The in-plane carbon bending vibrations are obtained from the non-degenerate $b_{1u}$ (1010 $cm^{-1}$) and degenerate $e_{2g}$ (606 $cm^{-1}$) moles of benzene. The $e_{2g}$ degenerate frequency in this case has been observed at 601 $cm^{-1}$. The carbon out-of-plane bending vibrations are defined by reference to the non-degenerate $b_{2g}$ (703 $cm^{-1}$) and degenerate $e_{2u}$ (404 $cm^{-1}$) modes of benzene. In the present case, the former is observed at 660 $cm^{-1}$ and the latter due to the degeneracy has been split into two non-totally symmetric components and the bands are observed at 464 and 438 $cm^{-1}$.

C—H *Vibrations*: The frequency of the C—H stretching vibrations of the methyl and methylene groups in the side chain do not differ very much from those found in the spectra of aliphatic compounds. They are not appreciably affected by the nature of the substituents. In the present study, they are obseved at 3060, 3039, 3028 and 3004 $cm^{-1}$ and they are in good agreement with Augus *et al.*[15] and Bailey *et al.*[16] Studies on the spectra of benzene show that there are two degenerate $e_{2g}$ (1178 $cm^{-1}$) and $e_{1u}$ (1037 $cm^{-1}$) and two non-degenerate $b_{2u}$ (1152 $cm^{-1}$) and $a_{2g}$ (1340 $cm^{-1}$) vibrations involving C—H in-plane bending vibrations. The frequencies 1274, 1260, 1228 and 1181 $cm^{-1}$ in 2-benzimidazole thione are assigned to C—H in-plane bending vibrations which belong to a′ species. These assignments are in agreement with values in literature.[17, 18]

The C—H out-of-plane deformations[19, 20] result from $b_{2g}$ (985 $cm^{-1}$), $e_{2u}$ (970 $cm^{-1}$), $e_{1g}$ (850 $cm^{-1}$) and $a_{2u}$ (671 $cm^{-1}$) modes of benzene and they are expected to occur in the region of 1000–600 $cm^{-1}$. The changes in the frequencies of these deformations from their values in benzene are almost determined exclusively by the relative position of the substituents and are almost independent of their nature[20, 21]. Hence the bands at 975, 869, 743 and 713 $cm^{-1}$ have been assigned to C—H out-of-plane bending vibrations.

N—H *Stretching*: Tsuboi[22] reported the N—H stretching frequency at 3481 $cm^{-1}$ in aniline. In line with his observation, N—H stretching is assigned to the band at 3417 and 3110 $cm^{-1}$ in the present work. The N—H in-plane bending and N—H out-of-plane deformations are assigned to bands at 1559 and 1375, and 705 and 615 $cm^{-1}$ respectively. This is in good agreement with the values assigned by Venkateswaran *et al.*[23] and Evans[24].

*C═S, C═N and C—N Vibrations*: The identification of the C—N stretching frequency in the side chains is a rather difficult task since there are problems in identifiying these frequencies from other vibrations. Pinchas *et al.*[25] assigned the C—N stretching band at 1368 $cm^{-1}$ in benzamide. With reference their value, the bands observed at 1358 and 1341 $cm^{-1}$ are assigned to C—N modes. Kahovec and Kohlrausch[26] identified the stretching frequency of the C═N bond in salicylic aldoxime at 1617 $cm^{-1}$. Hence, the bands at 1699 and 1659 $cm^{-1}$ are assinged to C=N modes. The bands at 1365 and 526 $cm^{-1}$ are assigned to C=S stretching and in-plane bending vibration respectively.

*Potential Energy Distribution (PED)*: To check whether the chosen set of vibrational frequencies contribute the maximum to the potential energy associated with normal coordinates of the molecule, the potential energy distribution has been calculated using the relation

$$\text{PED} = F_{ii}L_{ik}^2/\lambda_k$$

The close agreement between the observed and calculated frequencies confirms the validity of the present assignment.

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