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# Vibrational and Normal Coordinate Analysis of 2-Mercaptobenzothiazole

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The FTIR and FT Raman spectra of 2-mercaptobenzothiazole have been recorded and the normal coordinate analysis has been carried out by assuming $C_S$ point group symmetry. The 39 fundamental modes of vibrations are assigned based on the PED calculations.

## INTRODUCTION

The understanding of molecular structure requires good theoretical and high quality experimental approach in the study of polyatomic molecules. From the survey of the literature, it is evident that much emphasis has been given earlier on many coordination compounds with one or more sulphur atoms as coordinating centres. Some derivatives of imidazoles and thiazoles have interesting and useful biological properties. Moreover, they find applications in the drug design of herbicides and antivirus drugs[1,2]. Recent spectroscopic studies of benzothiazole and its derivatives have been motivated because the vibrational spectra are very useful for the understanding of specific biological processes and for the analysis of relatively complex systems. Consideration of these factors led us to undertake the detailed vibrational analysis of 2-mercaptobenzothiazole.

## EXPERIMENTAL

The pure polycrystalline sample of 2-mercaptobenzothiazole was obtained from Aldrich Chemical Company, USA and used as such without any further purification. The FTIR spectrum was recorded on Brucer IFS 66V model FTIR spectrophotometer using KBr pellets. The FT-Raman spectrum was recorded in the same instrument with necessary accessories. $Ar^+$ laser operating at 200 mw power exciting at 488 nm line was used as source.

The molecular structure of 2-mercaptobenzothiazole along with internal coordinates is shown in Fig. 1. By treating the ethyl group as point mass, the molecule under investigation belongs to $C_S$ point group symmetry. The 39 fundamental modes of vibration of the title compound are classified into 27 in-plane and 12 out-of-plane vibrations.

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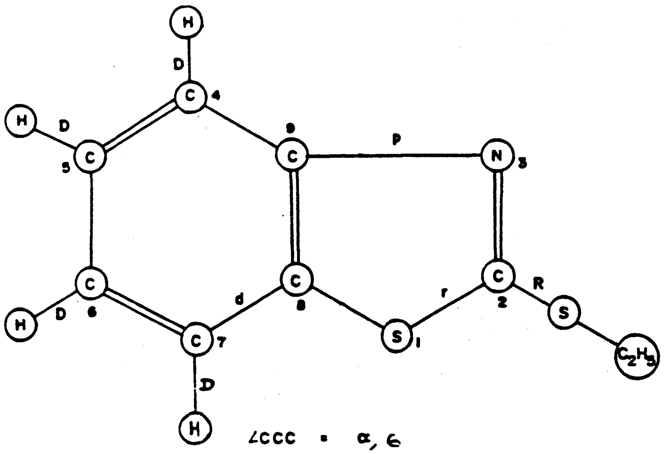

∠CCC = α, ∠CCN = β, ∠CSC = γ, ∠NCS = θ, ∠HCC = ψ, ∠CCC = ρ

Fig. 1. Molecular structure of 2-mercaptobenzothiazole and its internal coordinates

TABLE-1

VALENCE FORCE CONSTANTS OF 2-MERCAPTOBENZOTHIAZOLE

(Units: stretching:mdyne $Å^{-1}$; bending: mdyne $rad^{-1}$ and interaction constants:mdyne $Å^{-1}rad^{-2}$)

| Type of contants | Parameter | Coordinates | Value |
|---|---|---|---|
| Diagonal constants | | | |
| Stretching. | $f_D$ | C—H | 4.9025 |
| | $f_d$ | C—C | 3.9186 |
| | $f_r$ | C—S | 4.0511 |
| | $f_R$ | C—S | 3.6059 |
| | $f_P$ | C—N | 4.5159 |
| Bending | $f_\alpha$ | CCC | 0.7270 |
| | $f_\beta$ | CCN | 0.5971 |
| | $f_\gamma$ | CSC | 0.6613 |
| | $f_\theta$ | NCS | 0.5180 |
| | $f_\phi$ | HCC | 0.1891 |
| | $f_\rho$ | CCS | 0.1655 |
| Iteraction constants | | | |
| Stretch-Strech | $f_{dd}$ | CC CC | 0.2099 |
| | $f_{dp}$ | CC CN | 0.2019 |
| | $f_{dR}$ | CC CS | 0.1872 |
| | $f_{RP}$ | CS CN | 0.0961 |
| | $f_{RR}$ | CS CS | 0.0919 |
| | $f_{Dd}$ | CH CC | 0.1846 |
| Stretch-bend | $f_{D\alpha}$ | CH CCC | 0.1907 |
| | $f_{d\alpha}$ | CC CCC | 0.2115 |
| | $f_{R\alpha}$ | CS CCC | 0.1129 |
| | $f_{P\alpha}$ | CN CCC | 0.1047 |
| | $f_{R\theta}$ | CS NCS | 0.1029 |
| | $f_{R\phi}$ | CS HCC | 0.0841 |
| Bend-bend | $f_{\alpha\alpha}$ | CCC CCC | 0.0498 |
| | $f_{\alpha\phi}$ | CCC HCC | 0.0317 |
| | $f_{\alpha\gamma}$ | CCC CSC | 0.0291 |
| | $f_{\gamma\beta}$ | CSC CCN | 0.0265 |
| | $f_{\alpha\rho}$ | CCC CCS | 0.0211 |

The normal coordinate analysis has been performed by applying the procedures outlined by Wilson[3]. The structural parameters empolyed in the calculations were taken from Suttton's Table[4]. The initial set of force constants required to slove the secular equation $| FG - E \lambda | = 0$ were taken from the molecules of similar environment and they were subsequently refined using successive approximation and least square fit technique using the software developed by Schachtschneider[5] with necessary modifications. The potential energy distribution has also been calculated using the final set of force canstants in order to check the assignments proposed in the study.

## RESULTS AND DISCUSSION

**Force Constants:** The valence force constants of 2-mercaptobenzothiazole are presented in Table-1. A small variation in the values of the principal and interaction force constants of the title compound are due to the differences in the molecular parameters.

The $C_9$—$N_3$ ($f_p$) force constant of 2-mercaptobenzothiazole is found to be 4.5159 m dyne $Å^{-1}$ and this high value is due to the fact that the sulphur atoms of the compound will withdraw more electrons from nitrogen atom. Moreover, the sulphur hetero atom in the imidazole ring of 2-mercaptobenzothiazole will also change the electron density of the fused six member ring. Moreover the force constants $f_r$ and $f_R$ between carbon and sulphur atoms are found to be 4.0511 m dyne $Å^{-1}$ and 3.6059 m dyne $Å^{-1}$ respectively. The reason for the difference in these values can be explained that the $f_r$ between carbon and sulphur is within the ring of the system whereas $f_R$ between carbon and sulphur is in the second substituent position of the system. This also confirms that the electrons inside the rings are more delocalised. The high posistive value of interaction free constants obtained in this study also confirms the delocalization electrons in 2-mercaptobenzothiazole.

The observed and calculated frequencies and their potential energy distributions of the compound are presented in Table-2. The assignments of the observed bands are made in analogy with the group frequencies of hetero aromatic compounds. The maximum potential energy distribution obtained using the final set of force constants also confirms the present assignments.

The various vibrational modes observed for this hetero aromatic comound are discussed below.

**C—H vibrations:** The C—H stretching, C—H in-plane and C—H out-of-plane vibrations of the compound are identified in their characteristic regions. A narrow frequency shift in the absorption of the compound is due to intermolecular interactions. The assigments made for C—H vibrations are supported by literature[6–8]

**C—C vibrations:** The C—C vibrations of the compound are identified in the region 1641–1426 $cm^{-1}$. The Raman counterparts also occur in the same region. These assignments are made in accordance with the literature values[9].

**C—S vibrations:** In the spectroscopic investigation of 2-amino-6-nitrobenzothiazole, Mohan *et al.*[10] identified the C—S stretching at 1295 $cm^{-1}$. By analogy of Mohan's work, the FTIR bands at 1245 $cm^{-1}$ and the Raman bands at 1266 $cm^{-1}$ are assigned to C—S stretching vibrations in 2-mercaptobenzothiazole. These assignments are also in agreement with the assignments proposed by Martinez *et al.*[11]

TABLE-2
VIBRATIONAL ASSIGNMENT OF FUNDAMENTAL FREQUENCIES
($cm^{-1}$) of 2-MERCAPTOBENZOTHIAZOLE

| Species | FTIR | FT Raman | Calculated | Assignments (% PED) |
|---|---|---|---|---|
| a′ | — | 3120 ms | 3146 | C—H asymmetric stretching (98) |
| a′ | 3111 w | — | 3124 | C—H symmetric stretching (96) |
| a′ | 3078 w | — | 3085 | C—H stretching (95) |
| a′ | 3040 w | — | 3046 | C—H stretching (91) |
| a′ | 2962 w | — | 2989 | C—H stretching (97) |
| a′ | 1641 w | 1625 w | 1654 | C—C stretching (89) |
| a′ | 1596 ms | 1608 s | 1601 | C—C stretching (84) |
| a′ | 1497 vs | 1501 w | 1512 | C—C stretching (81) |
| a′ | 1457 s | 1474 w | 1479 | C—C stretching (87) |
| a′ | 1426 vs | 1419 w | 1433 | C—C stretching (91) |
| a′ | 1320 vs | 1318 s | 1318 | C—N stretching (94) |
| a′ | 1284 vs | — | 1271 | C—N stretching (88) |
| a′ | — | 1266 s | 1254 | C—S stretching (76) |
| a′ | 1245 ms | 1250 vs | 1234 | C—S stretching (74) |
| a′ | 1154 w | — | 1150 | C—H in-plane bending (70) |
| a′ | 1141 w | 1131 m | 1135 | C—H in-plane bending (69) |
| a′ | 1128 m | 1118 m | 1119 | C—H in-plane bending (71) |
| a′ | 1077 vs | — | 1061 | C—H in-plane bending (66) |
| a′ | 1035 vs | 1042 w | 1044 | Ring in-plane bending (61) |
| a′ | 1012 ms | 998 w | 1018 | C—C—C in-plane bending (73) |
| a′ | 938 w | — | 926 | C—C—C in-plane bending (67) |
| a′ | 868 w | — | 859 | C—N in-plane bending (64) |
| a′ | 848 w | — | 830 | C—N in-plane bending (69) |
| a″ | 792 w | — | 781 | C—H out-of-plane bending (55) |
| a″ | 751 vs | — | 766 | C—H out-of-plane bending (59) |
| a″ | 745 w | 745 w | 734 | C—H out-of-plane bending (61) |
| a″ | 668 vs |  | 679 | C—H out-of-plane bending (51) |
| a′ | 620 ms | 618 w | 611 | C—C—S in-plane bending (66) |
| a″ | 604 s | — | 589 | C—C—C out-of-plane bending (53) |
| a′ | 569 m | — | 555 | N—C—S in-plane bending (59) |
| a″ | 524 w | — | 511 | C—C—C out-of-plane bending (50) |
| a′ | 501 w | 499 w | 490 | C—S—C in-plane bending (67) |
| a″ | 485 w | — | 472 | Ring out-of-plane bending (49) |
| a″ | 424 s | — | 409 | C—C—C out-of-plane bending (44) |
| a′ | 394 vs | 397 vs | 382 | C—N—C in-plane bending (57) |
| a″ | 372 w | — | 366 | N—C—S out-of-plane bending (50) |
| a″ | 301 w | 301 w | 289 | C—N—C out-of-plane bending (54) |
| a″ | 233 m | 240 m | 226 | C—S—C out-of-plane bending (49) |
| a″ | 206 m | — | 197 | C—C—S out-of-plane bending (51) |

A small variation can be attributed to the vibrations involving interaction between C—S and C—N stretching vibrations.

**C—N vibrations:** The FTIR bands at 1320 and 1284 $cm^{-1}$ in 2-mecaptobenzothiazole are assigned to C—N stretching vibrations which are supported by the assignments of Yadav *et al.*[8] and Rai[12].

Apart from these assignments there are some more in-plane and out-of-plane bending vibrations presented in Table-2, made with the help of normal coordinate analysis. In addition to these identified bands there are some more peaks appearing in the recorded spectra in the lower and higher regions which are due to overtones and combination of bands.

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