

Study of Laser Raman Spectra of 2-Pyridyl Methyl Thiourea

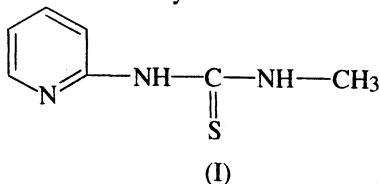
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Laser Raman spectra of 2-pyridyl methyl thiourea has been recorded. The characteristic vibrational frequencies of the pyridyl and NH groups and the aromatic rings have been identified by correlating the assignments with those available for related systems.

INTRODUCTION

2-Pyridyl methyl thiourea (2-PMTU) (I) is one of the simplest compounds of all alkyl substituted thioureas and analysis of its vibrational spectrum is important



as a starting point for the investigation of characteristic frequencies. The studies on thiourea derivatives are of interest because of their potential ability to coordinate either through sulphur or nitrogen. In general, pyridyl thioureas introduce a group with its own interesting chemistry and an additional element of geometrical isomerism about the-C (pyridyl)-N (thiouride) bond. Pyridyl thioureas are considered to be bio-chemically important¹. The investigations on aryl thioureas including methyl substitution are scarce²⁻⁴.

EXPERIMENT

The compound, was recorded on a Spex-Spectrometer using Ar⁺ laser source (5140Å) at 300 m.w. power.

RESULTS AND DISCUSSION

The planar compound (2-PMTU) contains 20 atoms to give rise to 54 vibrational modes of the free molecules. Only Raman bands of the compound observed are listed in Table 1. The symmetry C_s may be assumed for 36 a' in-plane and 18 a'' out of plane modes. Vibrational assignments is accomplished on the basis of those for constituent groups.⁵⁻⁸ Detailed assignments are available for N,N'-dimethyl thiourea⁹ and methyl pyridine¹⁰. Some prominent bands in the Raman spectra of N,N'-3 methyl thiourea¹¹ are found to have shifted in the

TABLE I
OBSERVED RAMAN BANDS AND THEIR MAIN ATTRIBUTIONS (cm⁻¹)

2-Pyridyl methyl thiourea (2-PMTU) Present work		NN' (3-methyl 2-pyridyl) methyl thiourea (Ref. 11)	
Frequency (cm ⁻¹)	Description	Frequency (cm ⁻¹)	Description
3070 (w)	NH Str	3095 (w)	NH Str
3055 (w)	NH Str	—————	—————
2985 (m)	CH Str (Py)	3040 (mw)	CH Str
2945 (w)	CH Str (Py)	3015 (mw)	CH Str
2895 (w)	CH ₃ Str (Py)	—————	—————
1602 (m)	Pyr ring Str	1605 (vvs)	Pyr ring Str
1588 (mw)	Pyr ring Str	1590 (m)	Pyr ring Str
1498 (m)	Pyr ring Str	1490 (s)	Pyr ring Str
1480 (w)	CN Str	—————	—————
1465 (w)	δ _s CH ₃ (Sym bend)	1475 (s)	δ _s CH ₃
1405 (w)	δ _s CH ₃ (Sym bend)	1400 (mw)	δ _s CH ₃
1330 (s)	δ _s NH v CN	1325 (vs)	δ _s NH, v CN
1295 (mw)	δ _s NH v CN	1285 (s)	δ _s NH, v CN
1240 (w)	δ CH Pyr	1250 (m)	δ CH
1165 (w)	δ CH	—————	—————
1150 (w)	N-CH ₃ Str	1165 (m)	N-CH ₃ Str
1130 (w)	CH ₃ Wag	—————	—————
1100 (mw)	π CH (Pyr)	1100 (m)	π CH Pyr
1048 (s)	CH ₃ rock	1075 (vs)	CH ₃ rock
990 (vvs)	ring breathing	950 (mw)	ring breathing
950 (w)	ring breathing	—————	—————
870 (w)	π CH Pyr	870 (mw)	π CH (Pyr)
850 (s)	(C=S) Str	—————	—————
775 (w)	π NH	780 (mw)	π NH
658 (w)	π NH	680 (mw)	π NH
618 (w)	ring def	635 (s)	ring def
515 (w)	ring def	551 (s)	ring def
400 (mw)	ring bend o.p.	395 (m)	ring bend o.p.
360 (w)	δ (C=S)	—————	—————
290 (w)	π (C=S)	—————	—————
250 (w)	δ CNC bend	250 (sh)	δ CNC (Py)
170 (mwb)	CH ₃ torsion o.p.	160 (s)	torsion o.p.

Note: str = stretching, δ = in-plane-bend, π = out-of-plane bend (O,P), m = medium, w = weak, s = strong, vvs = very very strong, sh = shoulder, v = str, δ_s = sym. deformation.

Raman spectra of 2-PMTU of the present work. This indicates the absence of methyl group in the pyridine ring of 2-PMTU in the present study. The NH stretching frequency in N, N'-dimethyl thiourea occurs at 3305 cm^{-1} in the solid⁹, at 3166 cm^{-1} in N-methyl thiourea¹² at 3095 cm^{-1} in N, N' (3 methyl, 2-Pyridyl) methyl thiourea¹¹ and at 3070 cm^{-1} in 2-PMTU of the present work. Similarly the frequency shifts are observed for pyridine rings (1605 cm^{-1})¹¹ and 1602 cm^{-1} in 2-PMTU of the present study. The other most intense band at 990 cm^{-1} corresponds to a ring breathing mode observed at 950 cm^{-1} in the Raman spectra of 2-PMTU. The assignments of others are represented in Table 1. The assignments of the work given in the Ref. (11) are also presented in Table 1 for comparative study.

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