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Normal Coordinate Analysis of 5-Methyl-2-Thiouracil

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The normal coordinate analysis of 5-methyl-2-thiouracil has been carried out by assuming C_S point group symmetry. The vibrational spectrum is interpreted on the basis of force field calculations and potential energy distributions.

INTRODUCTION

The vibrational spectra of various nucleic acid constituents including uracil have been reported in the literature[1–4]. The recent spectroscopic studies of uracil and its derivatives have been motivated by their biological and pharmaceutical importance[2]. The vibrational spectral analysis of 5-methyl-2-thiouracil reported in literature[5] was based only on comparisons with similar systems. It appears that no effort has been made by earlier workers to perform normal coordinate analysis to check the validity of the assignments. Hence a complete vibrational study of 5-methyl-2-thiouracil (Fig. 1) has been carried out to identify and assign the different modes of vibration based on normal coordinate analysis. Normal coordinate analysis and force field calculations are useful tools for interpreting the vibrational spectra.

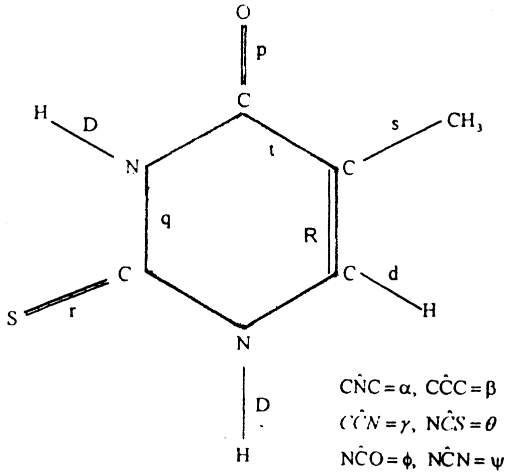

Fig. 1. Molecular structure of 5-methyl-2-thiouracil along with internal coordinates

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Molecular Symmetry

The structural formula along with internal coordinates of the molecule under investigation is shown in Fig. 1. If the methyl group is assumed as a single unit, the molecule under investigation belongs to C_s point group symmetry. The 30 fundamental modes of vibration are classified into 21 a′ and 9 a″ irreducible representations. The a′ and a″ species represent the in-plane and out-of-plane vibrations of the title compound.

Normal Coordinate Analysis

The normal coordinate analysis has been performed by applying Wilson's F-G Matrix mechanism[6] on the basis of General Valence Force Field (GVFF). The structural parameters required for the computation of G-Matrix are taken from Sutton's table[7]. The initial set of force constants required to solve the secular equation $|FG - E\lambda| = 0$ were taken from literature. All possible internal coordinates were included in the calculation of potential energy constants. The chief problem posed by this method lies in eliminating redundancies made in defining all the internal coordinates in the molecule. Branching redundancies can be readily eliminated by analytical procedures. However the occurrence of a ring gives rise to cyclic redundancies that cannot be readily eliminated analytically and usually call for numerical methods. Therefore the final set of force constants observed in this study are refined by least square fit technique and also by successive approximation method by using the software developed by Schachtschneider[8] with suitable modifications. To check whether the chosen set of assignments contributes maximum to the potential energy associated with normal coordinates of the molecule, the potential energy distribution calculation was made using the final set of force constants.

RESULTS AND DISCUSSION

The valence force constants obtained in the present investigation for 5-methyl-2-thiouracil are given in Table-1. The bond properties of uracil and its 5-substituted derivatives are influenced by the rearrangements of electron during substitution and addition reactions. The title compound undergoes tautomerism to give keto and enol forms.

The values of the force constants f_p (C═O) and f_r (C═S) are found to be 11.237 and 10.381 m dyne $Å^{-1}$ respectively which are in good agreement with double bond characteristic values reported in the literature. The correlation of stretching force constants between N—H, C—H, C—N, C—C and C═O bonds are given in Table-2. Small variations in the stretching force constants are mainly due to the molecular geometry and the nature of the substituents of these systems. The interaction force constants are slowly introduced in the force constants refinement process in order to minimise the difference between the observed and calculated frequencies. Moreover, in the computation of interaction force constants, CC CO, CN CO stretch-stretch interactions were added to obtain

TABLE-1
FINAL SET OF FORCE CONSTANTS OF A 5-METHYL-2-THIOURACIL
[IN UNITS OF m dyne Å^{-1}, m dyne rad^{-1} AND m dyne Å^{-1} rad^{-2}]

Type of constants	Parameters	Coordinates	Value
Stretching	f_D	N—H	6.047
	f_d	C—H	5.181
	f_p	C=O	11.237
	f_r	C=S	10.381
	f_R	C=C	8.329
	f_q	C—N	5.237
	f_s	C—C	4.169
	f_t	C—C	4.286
Bending	f_α	CNC	1.316
	f_β	CCC	0.669
	f_γ	CCN	1.055
	f_θ	NCS	1.183
	f_ϕ	NCO	0.992
	f_ψ	NCN	1.185
Stretch-stretch	f_{Dq}	NHCN	0.513
	f_{qq}	CNCN	0.246
	f_{qt}	CNCC	0.289
	f_{Rd}	CCCH	0.147
	f_{sR}	CCCC	0.115
	f_{ss}	CCCC	0.108
	f_{qr}	CNCS	0.394
	f_{qp}	CNCO	–0.723
	f_{tp}	CCCO	–0.506
	f_{dq}	CHCN	0.364
Stretch-bend	$f_{D\alpha}$	NH CNC	0.232
	$f_{d\alpha}$	CH CNC	0.257
	$f_{s\beta}$	CC CCC	0.167
	$f_{r\psi}$	CS NCN	0.316
	$f_{p\gamma}$	CO CCN	0.377
	$f_{q\alpha}$	CN CNC	0.207
Bend-bend	$f_{\alpha\alpha}$	CNC CNC	0.172
	$f_{\gamma\psi}$	CCN NCN	0.148
	$f_{\theta\psi}$	NCS NCN	0.166
	$f_{\beta\beta}$	CCC CCC	0.145
	$f_{\alpha\beta}$	CNC CCC	0.095

reasonable frequency fit in the double bond region. The negative value of the interaction force constants f_{qp} and f_{sp} indicates that the electrons are localised near their bonds. In general, the values of principal and interaction force constants obtained in the present investigation are fairly in agreement with the values of Arenus *et al.*[9]

TABLE-2

CORRELATION OF STRETCHING FORCE CONSTANTS (m dyne $Å^{-1}$) BETWEEN N—H, C—H, C—N, C—C AND C=O BONDS OF URACIL DERIVATIVES

Stretching coordinates	5-CU	5-AU	5-FU	5,2-MTU
N—H	6.050	6.247	6.069	6.047
C—H	5.034	5.381	5.137	5.181
C—N	5.826	5.972	5.620	5.237
C—C	3.162	3.619	4.716	4.169
C=O	11.397	11.135	11.195	11.237

5-CU: 5 Chloro uracil[10]; 5-AU: 5 Amino uracil[10]
5-FU: 5-Fluro uracil[10]; 5,2-MTU: 5-methyl-2-thiouracil

The observed and calculated frequencies along with the assignments of fundamentals and potential energy distribution for the title compound are given in Table-3.

N—H vibrations: The weak IR and Raman bands identified at 3240 and 3250 cm^{-1} respectively have been assigned to N—H stretching vibrations which are in agreement with the assignments available in the literature for uracil derivatives[10]. The assignments of in-plane and out-of-plane bending vibrations of N—H group are supported by the PED calculations.

C—H vibrations: The title compound 5-methyl-2-thiouracil gives rise to C—H stretching, C—H in-plane bending and C—H out-of-plane bending vibrations. The IR and Raman bands appearing at 3050 and 3070 cm^{-1} respectively have been assigned to C—H stretching vibrations. The C—H in-plane and out-of-plane bending vibrations have been found at 1020 and 585 cm^{-1} respectively. The above assignments are in good agreement with literature values and also supported by normal coordinate analysis[11].

C—N vibrations: The identification of C—N bands in the side chain is rather a difficult task, since there are problems in identifying these vibrations from other vibrations. In this study the IR bands at 1550, 1530, 1515 and 1485 cm^{-1} have been designated to C—N stretching vibrations. These assignments are supported by literature values[12].

C—C vibrations: The carbon-carbon stretching vibrations of the title compound have been observed at 1460 and 1380 cm^{-1}. The CCC trigonal in-plane and out-of-plane bending vibrations are assigned to the bands at 960 and 575 cm^{-1} respectively.

TABLE-3
VIBRATIONAL ASSIGNMENTS OF 5-METHYL-2-THIOURACIL ALONG WITH CALCULATED FREQUENCY (cm^{-1}) AND POTENTITAL ENERGY DISTRIBUTION

Species	IR frequency (cm^{-1}) and intensity	Raman frequency (cm^{-1}) and Intensity	Calculated frequency (cm^{-1})	Assignments (% PED)
a′	3240 vw	3250 w	3274	N—H stretching (99)
a′	3080 vw	3070 w	3107	C—H stretching (97)
–	2980 vw	–	–	CH_3 asymmetric stretching
–	2820 vw	–	–	CH_3 symmetric stretching
a	1640 vw	1650 vs	1666	C=O stretching (93)
a′	1550 vs	–	1575	C—N stretching (96)
a′	1530 m	–	1548	C—N stretching (98)
a′	1515 vw	1515 w	1527	C—N stretching (94)
a′	1485 vw	–	1502	C—N stretching (93)
a′	1460 s	1470 m	1481	C—C stretching (91)
a′	1380 s	1375 vs	1402	C—CH_3 stretching (97)
a′	–	1308 w	1322	C—C stretching (96)
a′	1280 m	–	1303	Ring in-plane stretching (92)
a′	1215 vsb	1223 s	1238	C=S stretching (98)
a′	1160 s	1168 s	1183	N—H in-plane bending (89)
a′	1140 vs	1142 m	1155	N—H in-plane bending (86)
–	1082 w	–	–	CH_3 rocking
a′	1020 w	–	1038	C—H in-plane bending (88)
a′	960 vw	965 m	973	C—C—C trigonal bending (86)
a′	820 vs	–	836	C—N in-plane bending (89)
a′	800 vw	–	814	N—C—O in-plane bending (84)
a′	–	763 vs	780	N—C—S in-plane bending (81)
a′	745 s	–	766	N—C—N in-plane bending (88)
a′	690 s	702 vs	714	C—N—C in-plane bending (82)
a″	655 m	662 m	668	N—H out-of-plane bending (74)
a″	–	593 vs	619	N—H out-in-plane bending (69)
a″	585 vs	–	602	C—H out-of-plane bending (66)
a″	575 w	–	561	C—C—C out-of-plane bending (64)
–	530 s	539 m	–	CH_3 torsion
a″	420 vw	422 s	436	C—N out-of-plane bending (58)
a″	410 vs	–	402	N—C—S out-of-plane bending (54)
a″	326 s	–	301	C—N—C out-of-plane bending (58)
a″	268 vw	–	249	N—C—O out-of-plane bending (56)
a″	230 vw	–	207	N—C—N out-of-plane bending (59)

w = weak; vs = very strong; s = strong; vw=very weak; m = medium

CH_3 group vibrations: The molecule under investigation has CH_3 group and hence the CH_3 group vibrations are possible in the vibrational spectra. The asymmetric and symmetric stretching vibrations of this group are identified at 2980 and 2820 cm^{-1}. The vibrations due to rocking and torsion modes of this group are also given in Table-2. The above assignments are supported by the assignments made by earlier workers[13].

The results of the normal coordinate analysis and PED calculations are very much useful in assigning the N—C—O, N—C—S, N—C—N and C—N—C in-plane and out-of-plane bending vibrations. The general agreement between the calculated and observed frequencies for both in-plane and out-of-plane modes is reasonable. The potential energy distributions based on the final set of force constants also support the vibrational analyses made in this study.

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