

Normal Coordinate Analysis of 5-Carbethoxy-2-thiouracil

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Normal coordinate analysis of fundamental vibrations of 5-carbethoxy-2-thiouracil has been carried out by assuming C_s point group symmetry. The potential energy constants are obtained by applying Wilson's FG matrix method. All the modes of vibrations are assigned and the potential energy distribution calculations are performed.

Key Words: Normal coordinate analysis, Carbethoxy thiouracil, Potential energy.

INTRODUCTION

Recent spectroscopic studies of uracil and its derivatives have been motivated by their biological and pharmaceutical importance. Uracil and its derivatives belong to the heterocyclic group. The N-heterocyclic molecules such as cytosine, pyrimidine, uracil and their derivatives are of immense importance, because some of them are the basic constituents of DNA and RNA and play an important role in the constitution properties of nucleic acids¹⁻⁴. The vibrational spectral analysis of 5-carbethoxy-2-thiouracil reported in the literature^{5,6} was based only on comparisons with similar systems. Further, all the genuine normal modes of vibrations appeared in the reported spectra of 5-carbethoxy-2-thiouracil was not analyzed and discussed in detail by the earlier workers. It appears that no effort has been made by the earlier workers to perform normal coordinate analysis to check the validity of the assignments. Hence, a complete vibrational study of 5-carbethoxy-2-thiouracil 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.

THEORY

Molecular symmetry: The molecular structure of 5-carbethoxy-2-thiouracil is shown in Fig. 1. The molecule is assumed to have C_s point group symmetry. The 57 fundamental modes of vibrations arising from 21 atoms are distributed into $39a^1$ and $18a^{11}$ irreducible representations. The a^1 and a^{11} species represent the in-plane and out-of-plane vibrations of 5-carbethoxy-2-thiouracil.

Normal coordinate analysis: The normal coordinate analysis for 5-carbethoxy-2-thiouracil has been performed on the basis of general valence force field (GVFF) by applying Wilson's FG matrix mechanism⁷. The structural parameters employed

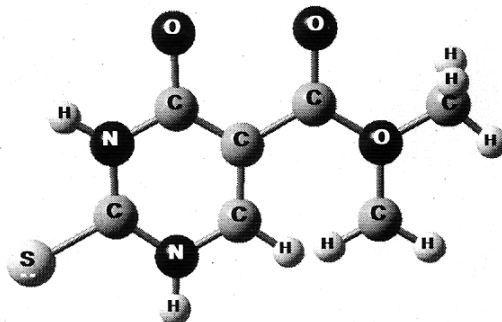


Fig. 1. Molecular structure of 5-carbomethoxy-2-thiouracil

in the calculations were taken from Sutton's table⁸. The initial set of force constants required to solve the secular equation were taken from the molecules of similar environment and those were subsequently refined by a least square fit technique using the software developed by Schachtschneider⁹ with suitable modifications. To check whether the chosen set of assignments contributes maximum to the potential energy associated with normal coordinate of the molecules, the potential energy distribution has been calculated using the final set of force constants.

RESULTS AND DISCUSSION

Force constants: The valance force constants obtained in the present investigations for 5-carbomethoxy-2-thiouracil is given in Table-1. The objective of the present study is to find out the stretching, bending and interaction force constants corresponding to each constituent and its position in the ring. The bonding properties of uracil and its 5-substituted derivatives are influenced by the arrangement of electrons during substitution and addition reactions.

The values of the force $f_{\text{O}}(\text{C}=\text{O})$ and $f_{\text{S}}(\text{C}=\text{S})$ are found to be 10.6526 and 9.1816 m.dyne \AA^{-1} , respectively. These values are in good agreement with the double bond characteristic values between carbon-oxygen atoms and carbon-sulfur atoms. The value of the force constants between carbon atoms in 5-carbomethoxy-2-thiouracil are found to be $f_{\text{R}} = 4.9480$ and $f_{\text{T}} = 4.0672$ m.dyne \AA^{-1} , respectively, which indicates that the C-C bond within the ring is more stronger than that of the C-C bond at the substitution position. The interaction force constants obtained in this study are quite reasonable and presented in Table-1. The interaction force constants are slowly introduced in the force constant refinement process in order to minimize the differences between the observed and calculated frequencies. The negative value of the interaction constants f_{RU} , f_{PU} , f_{UO} and f_{RO} indicate that the electrons are delocalized 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 obtained by the earlier workers on some similar types of molecules^{10,11}.

TABLE-1
 POTENTIAL ENERGY CONSTANTS OF A 5-CARBETHOXY-2-THIOURACIL
 [In the units of m.dyne Å⁻¹, m.dyne rad⁻¹; m.dyne Å⁻¹ rad⁻²]

Type of constants	Parameters	Coordinates	Value
Stretching	f_p	C-N	4.7195
	f_q	N-H	6.1947
	f_R	C-C	4.9480
	f_t	C-H	5.0411
	f_U	C=O	10.6526
	f_Q	C=S	9.1816
	f_r	C-C	4.0672
Bending	f_α	NCN	1.1852
	f_β	CNC	1.3164
	f_γ	CCC	0.6693
	f_ψ	NCC	1.0552
	f_ϕ	NCO	0.9927
	f_δ	NCH	0.6263
	f_ρ	NCS	1.1839
	f_θ	CNH	0.4915
Stretch – stretch	f_{pq}	CN NH	0.8019
	f_{pp}	CN CN	0.6504
	f_{pt}	CN CH	0.3649
	f_{RU}	CC CO	-0.5067
	f_{pU}	CN CO	-0.7231
	f_{pQ}	CN CS	0.3944
	f_{DD}	CO CO	0.7512
Stretch – bend	$f_{p\alpha}$	CN NCN	0.2462
	$f_{q\psi}$	NH NCC	0.1841
	f_{qp}	NH NCS	0.1519
	$f_{p\psi}$	CN NCC	0.1738
	$f_{Q\beta}$	CS CNC	0.1435
	$f_{p\delta}$	CN NCH	0.1108
	$f_{q\phi}$	NH NCO	0.2311
Bend – bend	$f_{\alpha\psi}$	NCN NCC	0.0436
	$f_{\beta\psi}$	CNC NCC	0.0518
	$f_{\beta\theta}$	CNC CNH	0.0432
	$f_{\delta\rho}$	NCH NCS	0.0411
	$f_{\theta\rho}$	CNH NCS	0.0306
	$f_{\phi\rho}$	NCO NCS	0.0296
	$f_{\theta\gamma}$	CNH CCC	0.0891

Vibrational assignments: The vibrational spectra of 5-carboxy-2-thiouracil have been analyzed by employing the normal coordinate calculations. The observed and calculated frequencies along with the vibrational assignments and the percentage of potential energy distribution are given in Table-2.

N-H Vibrations: According to Bellamy¹², the N-H stretching vibrations of aromatic compounds occur in the region 3500-3000 cm⁻¹. The IR bands observed at 3290

TABLE-2
VIBRATIONAL ASSIGNMENTS OF 5-CARBETHOXY-2-THIOURACIL

Species	IR* frequency (cm ⁻¹) and intensity	Raman* frequency (cm ⁻¹) and intensity	Calculated frequency	Assignments (%) PED
a ^I	3290 m	–	3280	N-H stretching (99)
a ^I	3249 m	–	3239	N-H stretching (98)
a ^I	3080 w	3070 w	3068	C-H stretching (99)
a ^I	3020 w	3010 w	3009	C-H asymmetric stretching (98)
a ^I	2930 w	–	2919	C-H asymmetric stretching (99)
a ^I	2920 m	–	2909	C-H symmetric stretching (98)
a ^I	2880 m	–	2869	C-H symmetric stretching (98)
a ^I	1730 m	1735 ms	1726	C=O stretching (89)
a ^I	1700 m	–	1696	C=O stretching (86)
a ^I	1630 w	1636 s	1625	C=C stretching (84)
a ^I	1622 w	–	1610	C-C stretching (99)
a ^I	1610 w	–	1598	C-C stretching (98)
a ^I	1589 w	–	1577	C-C stretching (99)
a ^I	1570 m	1572 s	1564	N-H in-plane bending (64)
a ^I	1535 m	–	1527	C-N stretching (80)
a ^I	1500 w	–	1492	C-N stretching (82)
a ^I	1487 ms	–	1479	C-H in-plane bending (76)
a ^I	1479 m	–	1471	C-H in-plane bending (80)
a ^I	1460 w	–	1452	Ring stretching (79)
a ^I	1452 w	–	1444	C-H in-plane bending (65)
a ^I	1440 w	–	1432	C-H in-plane bending (68)
a ^I	1423 w	–	1416	C-H in-plane bending (71)
a ^I	1370 vs	–	1363	C-N stretching (76)
a ^I	1329 m	–	1321	C-N stretching (77)
a ^I	1342 m	–	1334	C-O stretching (74)
a ^I	–	1314 ms	1308	C-O stretching (72)
a ^I	1223 s	1219 ms	1212	Ring in-plane bending (74)
a ^I	1160 vw	1168 s	1157	C=S stretching (83)
a ^I	1110 m	1110 m	1105	O-C-C in-plane bending (63)
a ^I	1070 m	1070 m	1060	C-C-C in-plane bending (89)
-	1040 w	1048 m	–	CH ₃ rocking
a ^{II}	975 vs	954 m	970	N-H out-of-plane bending (56)
a ^{II}	933 m	–	928	O-C-C out-of-plane bending (59)
a ^{II}	866 s	850 m	861	N-H out-of-plane bending (58)
a ^{II}	840 s	–	834	C-H out-of-plane bending (57)
a ^I	820 m	–	812	C-N in-plane bending (68)
-	790 m	–	–	CH ₂ rocking
a ^I	750 w	750 ms	744	N-C=S in-plane bending (61)
a ^I	731 ms	721 vs	728	C=O in-plane bending (64)
a ^{II}	682 w	–	679	C-C-C out-of-plane bending (53)
a ^I	670 w	671 w	665	C-N-C in-plane bending (64)
a ^{II}	658 ms	–	653	N-H out-plane bending (51)
a ^I	635 vw	635 w	633	C=S in-plane bending (69)

Species	IR* frequency (cm ⁻¹) and intensity	Raman* frequency (cm ⁻¹) and intensity	Calculated frequency	Assignments / % PED
a ^{II}	–	604 m	596	C-C-C out-of-plane bending (51)
a ^{II}	590 vs	–	582	Ring out-of-plane bending (51)
a ^{II}	–	570 w	565	C-H out-of-plane bending (56)
a ^I	525 vs	525 m	522	C-O-C in-plane bending (65)
a ^I	–	479 vs	474	C-N-C in-plane bending (66)
a ^{II}	450 w	–	448	C-O-C out-of-plane bending (48)
a ^{II}	423 m	–	404	C-N out-of-plane bending (55)
a ^{II}	390 m	386 w	388	C-O-C out-of-plane bending (45)
a ^I	364 w	–	358	N-C-S in-of-plane bending (68)
a ^{II}	329 m	335 ms	325	C-N-C out-of-plane bending (58)
a ^I	310 m	315 m	307	N-C-C in-of-plane bending (60)
a ^{II}	282 m	–	280	N-C-S out-of-plane bending (48)
a ^{II}	270 ms	260 m	267	N-C-C out-of-plane bending (51)
a ^{II}	258 vs	–	254	N-C-O out-of-plane bending (56)
a ^{II}	230 vs	235 vs	226	N-C-N out-of-plane bending (53)
a ^{II}	215 ms	–	211	C-N-H out-of-plane bending (51)
–	–	195 ms	–	Lattice vibrations

*Spectral data taken from Ref. 5 and 6.

and 3249 cm⁻¹ are assigned to N-H stretching modes of vibrations. The IR and Raman bands at 1572 and 1570 cm⁻¹ have been assigned to N-H in-plane bending vibrational modes. The N-H out-of-plane bending vibrations are identified at 975, 954, 866 and 850 cm⁻¹. These assignments are in agreement with assignments proposed by Krishnakumar *et al.*¹⁰.

C-N Vibrations: The identifications of C-N bands is highly complex since it is difficult to distinguish these vibrations from other vibrations. Krishnakumar *et al.*¹³ have assigned this mode at 1500, 1485 and 1371 cm⁻¹ in 5-methyl-2-thiouracil. In accordance with the above discussion, the IR bands at 1535, 1500, 1370 and 1329 cm⁻¹ in this study have been assigned to C-N stretching mode and the IR peaks at 820 and 423 cm⁻¹ are designated to C-N in-plane and out-of-plane bending vibrations, respectively.

C=S vibrations: The vibrations arising out of sulfur atom attached with carbon is of considerable importance, since the identification of the position of the C=S absorption has been a matter of difficulty. In organo-sulfur compounds hydrogen bonding effects may influence the absorption peaks. According to Bellamy¹², the symmetric frequency of C=S is within the range of 1160-1140 cm⁻¹. Hence, in this study the IR and Raman bands observed at 1168 and 1160 cm⁻¹ are assigned to C=S stretching vibrations.

C=O Vibrations: The carbonyl stretching frequency has been most extensively studied by infrared spectroscopy. This multiple bonded group is highly polar (>C^{δ+}=O^{δ-}) and therefore gives rise to an intense infrared absorption band. The carbon-oxygen

double bond is formed by $p\pi$ - $p\pi$ bonding between carbon-oxygen. Because of the different electro negativities of carbon and oxygen atoms, the bonding electrons are not equally distributed between the two atoms¹⁴. The following two resonance forms contribute to the bonding of the carbonyl group [$>C=O \longleftrightarrow >C^+-O^-$]. The lone pair of electron on oxygen also determines the nature of the carbonyl group. In the heteroaromatic compounds¹⁵, the carbonyl stretching frequencies are normally appeared in the region 1725-1705 cm^{-1} . By considering the above factors, the FTIR bands at 1730, 1700 cm^{-1} and Raman bands at 1735 cm^{-1} for 5-carbethoxy-2-thiouracil have been designated to C=O stretching modes of vibrations. The assignments proposed in this study for O-C-C, N-C-S, C-N-C, C-O-C, N-C-C, N-C-N and C-N-H bending vibrations are supported by the predominant values of potential energy distribution calculations.

Conclusion

A normal coordinate analysis has been performed that supports the assignments and reveals the mixing of the symmetric bending vibration of this molecule. Force constants in internal coordinate representation are compared well with their characteristics values. The calculated and observed frequencies agree well with the better frequency fit. The results confirm the ability of the methodology applied for interpretation of the 5-carbethoxy-2-thiouracil.

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