

## Vibrational Spectra and Normal Coordinate Analysis of 4-Amino Pyrazolo (3,4-d) Pyrimidine

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The FTIR and FT-Raman spectra of 4-amino pyrazolo (3,4-d) pyrimidine were recorded. The observed frequencies were assigned to various modes of vibrations on the basis of the normal coordinate analysis assuming  $C_s$  point group symmetry.

### INTRODUCTION

Pyrimidine and its derivatives are known for their biological and pharmaceutical importance. The spectroscopic study of the title compound is motivated because of its antifungal and antibacterial activities. The vibrational assignments reported in this paper are supported by the normal coordinate analysis based on General Valence Force Field (GVFF).

### EXPERIMENTAL

The pure 4-amino pyrazolo (3,4-d) pyrimidine (Fig. 1) was obtained from Fluka Chemie AG, Switzerland and used as such. The FTIR spectrum in KBr disc was recorded in the region  $4000\text{--}400\text{ cm}^{-1}$  using Bruker FTIR IFS 85 spectrophotometer. The FT-Raman spectrum of this molecule was recorded using 488 nm line of  $\text{Ar}^+$  laser for excitation, in the region  $4000\text{--}100\text{ cm}^{-1}$ . The normal coordinate calculations using Wilson's FG matrix<sup>1</sup> were performed by assuming the molecule belonging to  $C_s$  point group symmetry by treating the amino group as a single unit. The 30 normal modes of vibration are distributed as  $21a^1$  and  $9a^1$  types. The structural parameters employed in the calculations were assumed from Sutton's table<sup>2</sup>. The initial set of force constants required to solve the secular equation was taken from the systems of similar environment and they were subsequently refined by least square fit technique using the software developed by Mink and Mink<sup>3</sup>, with suitable modifications. To check the chosen set of vibrational assignments

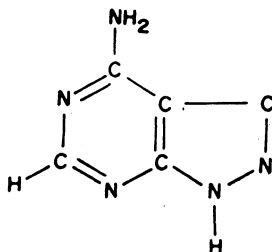


Fig. 1

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contributes maximum to the potential energy associated with normal coordinates of the molecule, the potential energy distribution has been calculated using the final set of force constants.

## RESULTS AND DISCUSSIONS

The final set of force constants obtained is presented in Table-1. The values of the force constants  $f_D(N-H)$ ,  $f_d(C-H)$  and  $f_p(C-N)$  are found to be in good agreement with the characteristic values. The difference between the force constants  $f_r$  and  $f_s$  between the carbon atoms is due to change in the structural parameters. The high positive value of the interaction force constants obtained for the title compound suggests that the electrons are highly delocalised. Hence, in the present study force constants of double bond character are not observed. The principal and interaction force constants reported in this paper are in good agreement with the literature values<sup>4-6</sup>.

The observed and calculated frequencies of 4-amino pyrazolo (3,4-d) pyrimidine along with their relative intensities, probable assignments and potential energy distributions obtained using final set of force constants are given in Table-2. The assignments made in this study are also supported by the normal coordinate analysis. The general agreement between the calculated and observed frequencies for both in-plane and out-of-plane mode is good.

**C—H vibrations:** The hetero-aromatic structure shows the presence of C—H stretching vibrations in the region  $3100-3000\text{ cm}^{-1}$ , which is the characteristic region for ready identification of C—H stretching vibrations<sup>7</sup>. In this region bands are not affected appreciably by the nature of substituents. Hence the FTIR band at  $3125\text{ cm}^{-1}$  and the FT-Raman band at  $3110\text{ cm}^{-1}$  in 4-amino pyrazolo (3,4-d) pyrimidine is assigned to C—H stretching mode. The C—H in-plane and out-of-plane bending vibrations are found at  $1184$  and  $760\text{ cm}^{-1}$  respectively. These assignments are in good agreement with the assignments of Rao<sup>8</sup>.

**C—C vibrations:** The C—C stretching vibrations of the title compound are found at  $1580$ ,  $1478$  and  $1462\text{ cm}^{-1}$ . The medium Raman and FTIR bands identified at  $1067$  and  $1049\text{ cm}^{-1}$  have been assigned to C—C—C in-plane bending vibrations. The out-of-plane bending vibrations of this group are shown in Table-2, which agree well with our earlier work<sup>4</sup> on similar type of compounds.

**C—N vibrations:** It is very difficult to identify the side chain C—N vibrations from other vibrations of the ring system. In the present investigation, the Raman bands observed at  $1394$ ,  $1309$  and  $1298\text{ cm}^{-1}$  have been assigned to C—N stretching vibrations. The IR counterparts are given in Table-2. These assignments are supported by the normal coordinate analysis and also in good agreement with the assignments of Mohan *et al.*<sup>9</sup>

**NH<sub>2</sub> group vibrations:** The N—H asymmetric and symmetric stretching vibrations of NH<sub>2</sub> group have been identified at  $3472$  and  $3406\text{ cm}^{-1}$  respectively. The bands appeared at  $1610$  and  $898\text{ cm}^{-1}$  are assigned to scissoring and wagging modes of amino group. The IR and Raman bands found at  $2410$  and  $2237\text{ cm}^{-1}$  are due to C—NH<sub>2</sub> asymmetric and symmetric stretching vibrations. The assignments for NH<sub>2</sub> group are made in accordance with the assignments suggested by Rao *et al.*<sup>10</sup> The stretching mode of N—H group present in the five-member ring of the

title compound has been identified at  $3306\text{ cm}^{-1}$ . The N—H in-plane and out-of-plane vibrations are found at  $1220$  and  $883\text{ cm}^{-1}$  respectively.

The IR bands observed at  $600$  and  $561\text{ cm}^{-1}$  are assigned to N—C—H and C—C—N out-of-plane bending vibrations, based on the normal coordinate analysis. Similarly the weak Raman bands appeared at  $538$  and  $338\text{ cm}^{-1}$  have been assigned to C—N—C and N—C—N out-of-plane bending vibrations.

TABLE-I  
INITIAL AND FINAL SET OF FORCE CONSTANTS OF 4-AMINO PYRAZOLO  
(3,4-d) PYRIMIDINE [IN UNITS OF m-dyne  $\text{\AA}^{-1}$ , m-dyne  $\text{rad}^{-1}$  AND m-dyne  $\text{\AA}^{-1}\text{ rad}^{-2}$ ]

Types of constants	Parameters	Coordinates	Initial value	Final value
Diagonal constants stretching	$f_D$	N—H	6.1302	6.1643
	$f_d$	C—H	5.0119	5.0317
	$f_p$	C—N	5.7521	5.7563
	$f_q$	N—N	6.1125	6.0859
	$f_r$	C—C	2.8506	2.8746
	$f_s$	C—C	2.8506	2.8622
Bending	$f_\alpha$	CCC	0.6284	0.6284
	$f_\beta$	CCN	0.3415	0.3406
	$f_\gamma$	CNC	0.2536	0.2609
	$f_\phi$	CNH	0.4915	0.4915
	$f_\psi$	NCH	0.2974	0.2766
	$f_\theta$	NCN	0.2586	0.2311
	$f_\delta$	CNN	0.2604	0.1995
Stretch-Stretch	$f_{Dp}$	NHCN	0.8019	0.8174
	$f_{Dq}$	NHNN	0.6108	0.6206
	$F_{pp}$	CNCN	0.6504	0.4261
	$f_{pr}$	CNCC	0.5119	0.3910
	$f_{rs}$	CCCC	0.0629	0.0895
	$f_{pq}$	CNNN	0.7501	0.7110
Stretch-Bend	$f_{D\delta}$	NH CNN	0.0845	0.0845
	$f_{d\theta}$	CH NCN	0.0551	0.0557
	$f_{p\beta}$	CN CCN	0.3169	0.3074
	$f_{D\theta}$	NH NCN	0.2014	0.2079
Bend-Bend	$f_{\gamma\delta}$	CNC CNN	0.0455	0.0455
	$f_{\alpha\gamma}$	CCC CNC	0.0397	0.0361
	$f_{\psi\theta}$	NCH NCN	0.0281	0.0197
	$f_{\phi\delta}$	CNH CNN	0.0411	0.0411

TABLE-2  
VIBRATIONAL ASSIGNMENTS OF 4-AMINO PYRAZOLO (3,4-d) PYRIMIDINE

Species	FTIR frequency (cm <sup>-1</sup> ) and intensity	FT-Raman frequency (cm <sup>-1</sup> ) and intensity	Calculated frequency (cm <sup>-1</sup> )	Assignments (%) PED
-	3472 m	-	-	N—H asymmetric stretching in NH <sub>2</sub> group
-	-	3406 w	-	N—H symmetric stretching in NH <sub>2</sub> group
a <sup>I</sup>	3306 w	-	3329	N—H stretching (98)
a <sup>I</sup>	3125 w	3110 w	3117	C—H stretching (99)
a <sup>I</sup>	2410 vw	-	2396	C—NH <sub>2</sub> asymmetric stretching (99)
-	2358 m	-	-	1425 + 933
a <sup>I</sup>	-	2237 vw	2251	C—NH <sub>2</sub> symmetric stretching (96)
a <sup>I</sup>	1674 ms	1670 vw	1681	C=N stretching (94)
-	-	1610 vw	-	NH <sub>2</sub> scissoring
a <sup>I</sup>	1593 s	-	1605	C—N stretching (96)
a <sup>I</sup>	-	1580 w	1576	C—C stretching (99)
a <sup>I</sup>	1493 ms	-	1486	C—NH <sub>2</sub> in-plane bending (92)
a <sup>I</sup>	-	1478 w	1466	C—C stretching (96)
a <sup>I</sup>	-	1462 w	1450	C—C stretching (97)
a <sup>I</sup>	-	1394 ms	1409	C—N stretching (96)
a <sup>I</sup>	1333 ms	1338 s	1346	N—C stretching (94)
a <sup>I</sup>	-	1309 m	1290	C—N stretching (96)
a <sup>I</sup>	-	1298 w	1285	C—N stretching (92)
a <sup>I</sup>	1220 vw	-	1234	N—H in-plane bending (77)
-	-	1202 vw	-	NH <sub>2</sub> rockings
a <sup>I</sup>	1184 vw	-	1196	C—H in-plane bending (68)
a <sup>I</sup>	-	1154 w	1170	C—N in-plane bending (66)
a <sup>I</sup>	-	1067 m	1084	C—C—C in-plane bending (64)
a <sup>I</sup>	1049 m	-	1061	C—C—C in-plane bending (62)
a <sup>I</sup>	-	1030 w	1042	N—C—N in-plane bending (68)
a <sup>II</sup>	933 w	939 w	930	C—NH <sub>2</sub> out-of-plane bending (56)
-	-	898 w	-	NH <sub>2</sub> wagging in NH <sub>2</sub> group
a <sup>II</sup>	883 w	-	866	N—H out-of-plane bending (59)
a <sup>II</sup>	760 w	-	744	C—H out-of-plane bending (58)
a <sup>II</sup>	720 vw	725 vs	698	C—C—C out-of-plane bending (64)
a <sup>I</sup>	702 vw	-	710	N—N stretching (79)
a <sup>II</sup>	613 m	615 m	616	C—C—C out-of-plane bending (57)
a <sup>II</sup>	600 vw	-	589	N—C—H out-of-plane bending (55)
a <sup>II</sup>	561 vw	-	551	C—C—N out-of-plane bending (56)
a <sup>II</sup>	-	538 w	528	C—N—C out-of-plane bending (52)
a <sup>II</sup>	-	338 w	321	N—C—N out-of-plane bending (58)
-	-	129 m	-	Lattice vibrations
-	-	113 w	-	Lattice vibrations

## REFERENCES

1. E.B. Wilson, *Phys. Rev.*, **45**, 706 (1934).
2. L.E. Sutton, *The Interatomic Bond Distances and Bond Angles in Molecules and Ions*, Chemical Society, London (1956).
3. J. Mink and J. Mink, *Computer Programme System for Vibrational Analysis of Molecules*, XXX, Erlangen (1983).
4. V. Krishnakumar, K. Parasuraman and A. Natarajan, *Indian J. Pure & Appl. Phys.*, **35**, 1 (1997).
5. S. Mohan and V. Ilangoan, *Indian J. Pure & Appl. Phys.*, **31**, 750 (1993).
6. J.F. Arenas, J.I. Marcos, M.A. Montaner and F.J. Ramier, *Spectrochim. Acta*, **46A**, 1721 (1990).
7. S. Mohan and V. Ilangoan, *Indian J. Pure & Appl. Phys.*, **32**, 91 (1994).
8. C.N.R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic Press, NY (1963).
9. S. Mohan and K. Settu, *Indian J. Pure and Appl. Phys.*, **32**, 189 (1994).
10. C.N.R. Rao and R. Venkataraghavan, *Canad. J. Chem.*, **42**, 43 (1964).

(Received: 25 August 2000; Accepted: 16 November 2000)

AJC-2193