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Normal Coordinate Analysis of 2,6-Diaminopurine

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The Fourier transform infrared spectrum of 2,6-diaminopurine was recorded. Normal coordinate analysis has been carried out by assuming C_s point group symmetry. Assignments to the observed bands are made. The potential energy distributions obtained in this study are also supporting the assignments.

Key words: Spectrophotometer, Normal coordinate analysis, potential enery disribution, 2,6-diaminopurine.

INTRODUCTION

The purine and its derivatives have been more extensively studied on account of their intrinsic interest as important biological compounds. The hydroxy and amino derivatives of purines are primarily studied, because of their existence in more than one form. The properties of purine bases are determined by their hydrogen and π bonding systems[1]. In the present investigation a complete vibrational study for 2,6-diaminopurine has been carried out for the first time based on the normal coordinate analysis. Normal coordinate analysis and force field calculations are useful tools for interpreting the vibrational spectra.

EXPERIMENTAL

The pure sample of 2,6-diaminopurine (Fig. 1) was obtained from Fluka Chemie AG, Switzerland and used as such. The FTIR spectrum in KBr disc was recorded in the region 4000–400 cm^{-1} using Bruker FTIR IFS 66V spectrophotometer. The Bruker IFS FTIR instrument consists of globar and mercury vapour lamps as sources, an interferometer chamber comprising of KBr and mylar beam splitters followed by a sample chamber and detector. The spectrophotometer works under vacuum conditions. The instrument has a resolution of 0.1 cm^{-1}. Signal averaging, signal enhancement, base line correction and other spectral manipulations are possible with multitasking OPUS software on the dedicated PC/AT 486. The transformation of the interferogram into spectrum is carried out mathematically using Fourier transform algorithm.

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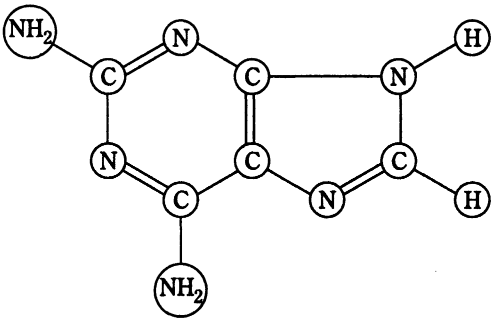

Fig. 1. Molecular structure of 2,6-diaminopurine

Normal Coordinate Analysis

The normal coordinate calculations using Wilson's[2] FG matrix mechanism were perfomed by assuming the molecule belonging to C_s point group symmetry by treating the amino groups as single units. The 33 normal modes of vibrations are distributed as 23 a′ and 10″ types. The structural parameters employed in the calculations were taken from Sutton's table[3]. The initial set of potential enegy constants to solve the secular equation $|FG - E\ \lambda| = 0$ were taken from the literature[4]. The main problem posed by this method lies in eliminating redundancies made in defining all the internal coordinates of this 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 potential energy constants are refined by least square fit algorithm by using the software developed by Mink and Mink[5] with suitable modifications.

RESULTS AND DISCUSSION

The potential energy constants obtained in the present study for 2,6-diaminopurine are given in Table-1. Pyrimidine ring in purine molecule withdraws electrons from the imidazole ring of purine. This is due to resonance hybridization and hence there is no pure double bond existing either in carbon-carbon or in carbon-nitrogen atoms. Therefore, the electrons in this system are highly delocalised. The values of f_p, f_q and f_r between C—N bond are found to be larger than between C—H bond (f_d). This suggests that C—N bond is stronger than C—H bond. The decreasing trend in C—N values is due to change in the values of the structural parameters. The final set of principal and interaction constants obtained in this study are in good agreement with the literature values[6–8].

The observed and calculated frequencies of 2,6-diaminopurine along with potential energy distribution are given in Table-2.

TABLE-1
POTENTIAL ENERGY CONSTANTS OF 2,6-DIAMINOPURINE
(in the units of m-dyne A^{-1}, m-dyne rad^{-1} and m-dyne A^{-1} rad^{-2})

Types of constants	Parameter	Coordinates involved	Value
Stretching	f_D	N—H	6.173
	f_d	C—H	4.985
	f_p	C—N	5.628
	f_q	C—N	5.319
	f_r	C—N	5.110
	f_s	C—C	3.271
Bending	f_a	NCN	0.953
	f_β	NCC	0.815
	f_g	CNC	0.648
	f_δ	NCH	0.418
	f_θ	CCC	0.591
	f_ϕ	CNH	0.295
Stretch-stretch	f_{Dq}	NHCN	0.891
	f_{dq}	CHCN	0.185
	f_{pp}	CNCN	0.560
	f_{ss}	CCCC	0.429
	f_{sp}	CCCN	0.386
	f_{sr}	CCCN	0.337
Stretch-bend	f_{Da}	NH NCN	0.294
	f_{Dg}	NH CNC	0.215
	f_{da}	CH NCN	0.269
	f_{qa}	CN NCN	0.137
	$f_{q\beta}$	CN NCC	0.107
	$f_{p\theta}$	CN CCC	0.094
	f_{sg}	CC CNC	0.081
Bend-bend	$f_{a\beta}$	NCN NCC	0.177
	$f_{a\theta}$	NCN CCC	0.141
	f_{gg}	CNC CNC	0.137
	$f_{g\delta}$	CNC NCH	0.046
	$f_{g\theta}$	CNC CCC	0.031

Amino group vibrations: The N—H stretching vibrations of the amino group have been identified at 3341 cm^{-1}. The bands appearing at 1662, 1145, 688 and 257 cm^{-1} in the FTIR spectrum have been assigned to scissoring, twisting, wagging and torsion modes of NH_2 group. The assignments made for this group are also supported by the literature values[9].

C—H vibrations: The heteroaromatic structure shows the presence of C—H stretching vibrations in the region 3100-3000 cm^{-1} which is the characteristic region for the ready identfication of this group[10]. In this region the bands are not much disturbed due to substituents. Hence, in the present study the FTIR bands at 3087 and 2963 cm^{-1} have been assigned to C—H stretching modes of vibrations.

TABLE-2
OBSERVED AND CALCULATED FREQUENCIES OF 2,6-DIAMINOPURINE

Symmetry species	FTIR observed frequency (in cm^{-1}) and intensity	Calculated frequency (in cm^{-1})	Assignments (% PED)
–	3341 ms	–	N—H stretching in NH_2 group
a′	3204 ms	3192	N—H stretching (94)
a′	3087 w	3073	C—H stretching (92)
a′	2963 w	2951	C—H stretching (86)
a′	1717 vs	1703	C—N stretching (86)
–	1662 w	–	NH_2 scissoring
a′	1616 w	1624	C—C stretching (78)
a′	1606 w	1618	C—C stretching (72)
a′	1582 w	1602	C—C stretching (69)
a′	1554 w	1542	C—C stretching (64)
a′	1530 m	1516	C—N stretching (76)
a′	1477 m	1468	C—N stretching (76)
a′	1439 m	1422	C—N stretching (72)
a′	1395 m	1381	C—N stretching (74)
a′	1335 w	1326	C—NH_2 asymmetric stretching (76)
a′	1290 w	1279	C—NH_2 symmetric stretching (71)
a′	1227 m	1216	N—H in-plane bending (69)
–	1145 w	–	NH_2 twisting
a′	1113 s	998	C—H in-plane bending (67)
a′	984 m	972	C—C—C in-plane bending (65)
a′	967 w	959	C—C—C in-plane bending (69)
a″	883 w	870	N—H out-of-plane bending (60)
a″	856 w	861	C—H out-of-plane bending (60)
a″	846 w	830	C—C—C out-of-plane bending (64)
a″	766 w	754	C—C—C out-of-plane bending (62)
a′	733 w	726	C—N in-plane bending (61)
–	688 w	–	NH_2 wagging
a″	670 w	652	N—C—C out-of-plane bending (59)
a″	646 w	637	C—N—C out-of-plane bending (52)
a″	618 ms	602	C—N—H out-of-plane bending (51)
a′	595 w	581	N—C—N in-plane bending (56)
a″	551 w	542	C—N out-of-plane bending (49)
a′	492 w	487	C—NH_2 in-plane bending (51)
a′	446 w	421	N—C—H in-plane bending (48)
a′	385 w	365	C—NH_2 in-plane bending (42)
a″	317 w	297	C—NH_2 out-of-plane bending (47)
–	257 w	–	NH_2 torsion
a″	201 w	192	N—C—N out-of-plane bending (49)

C—N vibrations: The identification of C—N bands in the side chain is a very difficult task, since overlapping of bands is possible in this region. However, the results of the normal coordinate analysis will be useful to overcome this difficulty. Hence, the medium FTIR bands appearing at 1530, 1477, 1439 and 1395 cm^{-1} have been assigned to C—N stretching.

Conclusion

The potential energy constants reported here would help to understand the physical and chemical properties of purines and its derivatives. The general agreement between the in-plane and out-of-plane vibrations are good. The high positive value of the interaction force constant indicates that the electrons in this system are highly delocalized. Apart from the characteristic bands, some more bands identified in the FTIR spectrum are due to overtones and combination of bands.

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