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Electronic Absorption Spectra of 2-Amino-3,5-Dichloro-2,6-Difluoro-Pyridine and 2-Hydroxy-5-Nitro Pyridine

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The near ultraviolet absorption spectra of 2-amino-3,5-dichloro-2,6-difluoro pyridine and 2-hydroxy-5-nitropyridine in the vapour phase have been recorded on Beckman DK-2A and a detailed vibronic analysis is presented. They are found to exhibit one band system corresponding to $^1A_{1g} \rightarrow {}^1B_{1u}$(2100 Å) transition and two systems of bands arising from $^1A_{1g} \rightarrow {}^1B_{2u}$ (2600 Å) and $^1A_{1}g \rightarrow {}^1B_{1u}$ (2100 Å). Transition of benzene has been identified for 2-amino-3,5-dichloro-2,6-difluoropyridine and 2-hydroxy-5-nitropyridine. The spectra have been analysed assuming Cs point group for each molecule. The assignments have been interpreted in terms of ground and excited state fundamental frequencies to the probable modes of vibration. The correlation to the IR fundamentals for both the molecules and the red shift of 0, 0 bands have also been presented.

INTRODUCTION

The electronic spectra of pyridine and some of its mono- and di-substituted pyridines have been studied extensively in recent yea-s.[1–13]

Kasha[14] suggested that the electronic transitions in pyridine exhibit two band systems in the near UV region, one towards the longer wavelength side designated as n-π* transition and other towards the shorter wavelength side as π-π* transition analogous to 2600 Å ($^1A_{1g} \rightarrow {}^1B_{2u}$) system of benzene. These systems arising respectively from the excitation of a π-electron and a nitrogen non-bonding (sp^2) electron to the unoccupied π-orbitals[15–17].

Mochizuki[18] has made a systematic study of the electronic absorption spectra of pyridine and its deuterated analogues. The n-π* is however absent in the spectra of substituted halogen pyridine because of large inductive influence of halogen atom on the sp^2 electron on the nitrogen atom of the ring[19–23]. But recently Srivastava and Prasad[24] have observed a band corresponding to n-π* transition around 3300Å in 2-chloro-3-pyridinol. The electronic spectra of substituted amino, hydroxy and nitro pyridines also appear in literature.[25, 26] Praveen *et al.*[27, 28] have reported the infrared spectra of 2-amino-3,5-dichloro-2, 6-difluoropyridine and 2-hydroxy-5-nitro pyridine.

The study the spectral changes produced due to two or more interacting groups attached to the ring at various positions, as also to study the low frequency fundamentals, correlation to IR modes, red shift and to make the assignments unequivocal, the present study has been undertaken to report near ultraviolet spectrum and assignments to ground and excited state fundamentals, corresponding to all modes of vibrations of 2-amino-3,5-dichloro-2,6-difluoro pyridine and

2-hydroxy-5-nitropyridine. It appears that no previous report has been found on the electronic spectra of both the molecules cited above.

EXPERIMENTAL

The spec-pure grade samples of 2-amino-3,5-dichloro-2,6-difluoro pyridine (2,3,5,2,6-ADCDFP) and 2-hydroxy-5-nitropyridine (2,5-HNP) were obtained from Sigma-Aldrich Co. and used as such as received. The vapour phase near UV absorption spectra of both the molecules have been recorded on Beckman DK-2A. The experimental procedure for recording and studying the UV absorption spectrum in vapour state was the same as described elsewhere[1, 6, 7].

RESULTS AND DISCUSSION

The wave number of the vibrionic bonds (both ground state and electronic state fundamentals) with their approximate intensities and probable assignments for both the molecules (2,3,5,2,6-ADCDFP and 2,5-HNP) are listed in Tables 1 and 3. For correlation, the observed electronic ground and excited state fundamental frequencies together with the reported infrared frequencies are collected in Tables 2 and 4 separately, while the red shift of 0, 0 band compared to benzene along with that of some similar molecules are presented in Table-5.

TABLE-1
ANALYSIS OF THE ELECTRONIC ABSORPTION BANDS OF
2-2-AMINO-3,5-DICHLORO-2,6-DIFLUORO PYRIDINE

Wave number (cm^{-1}) Relative intensity†	Shift from (0, 0) band (cm^{-1})	Assignment
	$^1A_{1g} \rightarrow {}^1B_{1u}$ (2100 Å) system	
40160 s	0 – 823	0 – 823
40322 s	0 – 661	0 – 2× 332
40485 ms	0 – 498	0 – 2× 249
40650 ms	0 – 333	0 – 333
40 983 vs	0, 0	0, 0
41152 vw	0 + 169	0 + 169
41322 s	0 + 339	0 + 339
41493 ms	0 + 510	0 + 2× 255
41666 mw	0 + 683	0 + 683
41841 s	0 + 858	0 + 1211 – 333
42194 ms	0 + 1211	0 + 1211
42372 mw	0 + 1389	0 + 1389
42735 ms	0 + 1752	0 + 1752
42918 m	0 + 1935	0 + 3× 683
43478 ms	0 + 2495	0 + 2495
43658 vw	0 + 2675	0 + 2× 1211 + 255
44052 s	0 + 3069	0 + 2× 1211 + 683

†vw = very weak, mw = medium weak, s = strong, ms = medium strong, vs = very strong
Ref.: 1, 3, 29, 30

All interpretations are based assuming Cs point group for both the molecules. Thus there will be only two types of electronic levels, those which are symmetric to molecular plane and those which are antisymmetric to it. Under reduced symmetry Cs, the forbidden transition of benzene $^1A_{1g} \rightarrow {}^1B_{2u}$ (2600 Å) and $^1A_{1g} \rightarrow {}^1B_{1u}$(2100 Å) correspond to the allowed type $A^1 \rightarrow A^1$ transition with the transition moment lying in the plane of the molecule. It is expected that only symmetric vibrations of the molecules should appear with sufficient intensity. The vapour phase spectra for both the molecules are discussed separately.

Spectra in vapour phase for 2,3,5,2,6-ADCDFP

The absorption spectra of 2,3,5,2,6-ADCDFP under different vapour pressures and at different absorption path lengths show only one system of band and it is attributed to the $^1A_{1g} \rightarrow {}^1B_{1u}$ transition. As seen from Table-1, it shows somewhat broad but well resolved vibronic bands; of these the highly intense band at 40983 cm^{-1}, which is found to persist with sufficient intensity at a low pressure of the absorping vapour, is identified as the 0, 0 band of the system. On the shorter wavelength side of 0, 0 band there appear strong to medium intensity bands which are shifted by 339, 510, 858, 1211, 1752, 2495, 3069 from 0, 0 band and are assigned as the fundamentals in the excited state *i.e.* upper electronic state. Similarly the vibrionic bands on the longer wavelength side of the 0, 0 band with spacing 333, 498, 661, 823 cm^{-1} are identified as the ground state fundamentals. The above work agrees with literature[29, 30].

The close agreement of the ground and excited state fundamental has been observed in the UV absorption spectra with the reported IR frequencies of the molecules. All observed bands have been explained as overtones or combination bands of these fundamentals. As seen from Table-2, the upper state fundamental at 638 cm^{-1} has been correlated to G.S. fundamental at 661 cm^{-1} and assigned to C—C in-plane bending. It can be seen that the E.S. value at 339 cm^{-1} has been correlated to G.S. value and attributed as C—Cl in-plane bending. While the E.S. value at 1211 cm^{-1} is attributed to C—H stretching, all values are in agreement with IR values.[27]

TABLE-2
CORRELATION OF THE FUNDAMENTAL VIBRATIONAL FREQUENCIES OF 2-AMINO-3,5-DICHLORO-2,6-DIFLUORO-PYRIDINE. IN INFRARED SPECTRA (cm^{-1}) AND ULTRAVIOLET SPECTRA (cm^{-1}) AND THEIR ASSIGNMENT

IR[27]	$^1A_{1g} \rightarrow {}^1B_{1u}$(2100 Å) system		Assignment$_{(a)}$[27]
	G.S.	E.S.	
384	333	339	β (C—Cl)
625	661	683	β(C—C)
811	823	858	γ(N—H)
1228	–	1211	ν(C—H)
1370	–	1389	Ring stretching

(a) All values with symbol taken from Ref. 27

The works above cited are well in agreement with the present literature.[1, 3, 31,]

TABLE-3
ANALYSIS OF THE ELECTRONIC ABSORPTION BANDS OF 2-HYDROXY-5-NITRO PYRIDINE

Wave number (cm^{-1}) Relative intensity†	Shift from (0, 0) band (cm^{-1})	Assignment‡
$^1A_{1g} \rightarrow {}^1B_{2u}$ (2100 Å) system I		
31928 ms	0 – 1405	0 – 1405
32216 mw	0 – 1117	0 – 406 × 2 + 308
32362 m	0 – 971	0 – 971
32573 mw	0 – 760	0 – 760
32658 ms	0 – 675	0 – 504 + 166
32829 s	0 – 504	0 – 504
32927 mw	0 – 406	0 – 406
33333 vvs	0, 0	0, 0
33436 ms	0 + 103	0 + 103
33659 vvw	0 + 326	0 + 326
33727 s	0 + 394	0 + 326 + 83
33944 ms	0 + 611	0 + 611
34014 s	0 + 681	0 + 681
34231 ms	0 + 898	0 + 898
34341 m	0 + 1008	0 + 681 + 326
34620 m	0 + 1287	0 + 898 + 394
34732 vw	0 + 1399	0 + 2 × 681
34953 mw	0 + 1620	0 + 2 × 760 + 103
47169 w	0 – 1374	0 – 2 × 697
47393 ms	0 – 1150	0 – 924 + 2 × 234
47619 s	0 – 924	0 – 697 + 234
47846 ms	0 – 697	0 – 697
48076 ms	0 – 467	0 – 467
48309 ms	0 – 234	0 – 234
48543 vvs	0, 0	0, 0
48780 s	0 + 247	0 + 247
49019 vs	0 + 476	0 + 2 × 247
49261 mw	0 + 718	0 + 476 + 247
49504 ms	0 + 961	0 + 718 + 247
49751 s	0 + 1208	0 + 961 + 247

†Symbols taken from Table-1.
‡Ref. = 2, 3, 5, 7, 11, 12, 13, 29.

Vapour Phase Spectra of 2,5-HNP

In conformity to the allowed nature of the transition and nature of the observed absorption spectrum in vapour phase recorded at different lengths of the absorbing path and different temperature, the molecule 2,5-HNP shows two distinct fairly

intense systems (systems I and II) of bands. On the basis of the similar assignments in case of pyridine[12, 14, 21, 22, 34], the 1st band system starting from about 33333 cm^{-1} is designated as $^1A_{1g} \rightarrow {}^1B_{2u}$ (2600 Å) system and the 2nd system of bands which extends from 48543 cm^{-1} towards the shorter wavelength side is attributed to $^1A_{1g} \rightarrow {}^1B_{1u}$ (2100 Å) transition.

1st System: It is seen from Table-3 that the band system lying on the higher wavelength side consists of well resolved bands which are somewhat broad, of which the very strong band observed at 33333 cm^{-1} is identified as the 0, 0 band. This is similar to the literature value[1, 3, 18, 26, 29]. This band continues to appear with appreciable intensity even at a very low pressure of the absorbing vapour. The vibronic bands are of diffuse type and degraded to the red. On the shorter wavelength side of 0, 0 band, there are found some good bands which are separated from it by 103, 394, 611, 681, 898 cm^{-1}. These are identified as excited state fundamentals. The vibronic bands lying on the higher wavelength side of 0, 0 band with spacing 504, 675, 1405 cm^{-1} are attributed to ground state fundamentals. It is seen from Table-4 that the E.S. and G.S. fundamental frequencies observed in UV absorption spectrum closely agree with the IR shift.[28] All other bands in the spectrum are explained as the overtones or combination bands of the fundamental frequencies. The G.S. values at spacing 406 cm^{-1} and 504 cm^{-1} are well assigned as (C—C) out-of-plane bending and (O—H) out-of-plane bending with IR values respectively.

TABLE-4
CORRELATION OF THE FUNDAMENTAL VIBRATIONAL FREQUENCIES OF 2-HYDROXY-5-NITRO PYRIDINE IN INFRARED AND ULTRAVIOLET SPECTRA AND THEIR ASSIGNMENT

(All values in cm^{-1})

$IR_{(b)}$[28]	2600 Å System-I		2100 Å System-II		Assignement$_{(b)}$[28]
	G.S.	E.S.	G.S.	E.S.	
452	406	–	467	476	(C—C) o.p.b.
560	504	–	–	–	(O—H) o.p.b.
625	675	611	697	–	(C—C) i.p.b.
742	760	–	–	718	Ring breathing
867	–	898	–	–	(C—H) o.p.b.
915	–	–	924	–	(C—H) o.p.b.
995	971	–	–	961	Trigonal bending
1155	1117	–	1150	–	(C—H) i.p.b.
1225	–	–	–	1208	(O—H) i.p.b.
1282	–	1287	–	–	(C—C) stretching
1375	–	1399	1374	–	Ring stretching
1445	1405	–	–	–	(C—C) stretching
1625	–	1620	–	–	Ring stretching

o.p.b.—out-of -plane-bending
i.p.b.—in-plane-bending.

The bands involve E.S. value at 675 cm^{-1} correlated with G.S. value at 611 cm^{-1} in accordance with IR value at 625 cm^{-1}which has been identified as (C—C) in-plane bending. The G.S. value at the interval 971 cm^{-1} is assigned as C—H in-plane bending while the E.S. value at the interval 898 cm^{-1} is well attributed to (C—H) out-of-plane bending with IR value. The other group vibrations are well interpreted in Table-4. The present work described above with experimental values is in well agreement with several workers.[4–7, 11, 12, 29, 31, 32]

2nd *System:* In addition to the system of bands described above another strong system of bands with a few vibrionic structures is observed in the absorption spectrum under $^1A_{1g} \rightarrow {}^1B_{1u}$ (2100 Å) transition of benzene in the present case. It is likely that this system of bands corresponds to the system of bands observed in the same region or sequence[17, 33, 35, 36]. The strong band observed at 48543 cm^{-1} is taken as the 0, 0 band and the other bands towards the lower wavelength side of 0, 0 band with spacing 247, 476, 961, 1208 cm^{-1} are assigned as the excited state fundamentals. The bands observed on the higher wavelength side of the 0, 0 band and separated by 234, 467, 924, 1150 cm^{-1} are interpreted as the ground state fundamentals. The G.S. and E.S. values of this system also show the correlation with the IR fundmentals which are well given in Table-4. The assignment of this band system is in agreement with the earlier assignment in case of gaseous pyridine[17] and other substituted pyridines[11–13] and others.

TABLE-5
POSITION OF 0, 0 BANDS AND RED SHIFT FOR 2,3,5,2,6-ADCDFP AND 2,5-HNP

Molecule	Position of 0, 0 band (cm^{-1})	Shift with respect to benzene (cm^{-1})	Reference
Benzene	38089	–	30
Toluene	37480	609	30
2,3,5,2,6-ADCDFP	–	–	present work
2,5-HNP	33333	4756	present work
6-Amino-2-methylpyridine	34133	3956	3
2, 3-Dichloro pyridine	35585	2504	2
2, 6-difluore pyridine	37522	567	6
2-Fluoro-2	36107	1982	30

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Shift of the 0, 0 band

Kasha,[14] Sponer[15] and Rush[16] showed that the 0, 0 band of the π-π system of pyridine appears at 38350 cm^{-1} in vapour phase. The molecule 2,3,5,2,6-ADCDFP shows no red shift. But in 2,5-HNP, the 0, 0 band has been identified at 33333 cm^{-1}. It shows that the band system has been shifted towards the longer wavelength side by 5017 cm^{-1} with respect to pyridine. Similar red shift has been reported by previous workers.[24 29 30 35] Comparison of the red shift with respect to benzene are shown in Table-5 for both the molecule, substituted pyridines and other compounds.

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