

Infra-red Spectral Investigations on 2,4-Dinitrophenyl Hydrazine

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In this work, we report an analysis of vibrational spectrum of 2,4-dinitrophenyl hydrazine. Infrared spectrum of 2,4-dinitrophenyl hydrazine has been recorded in the region of $4000\text{--}400\text{ cm}^{-1}$. The spectrum of this reagent has been analysed on the basis of C_2 symmetry.

INTRODUCTION

The vibrational spectra of biologically important pyridine derivatives have been examined previously,^{1–4} but the interpretation of these compounds due to high complexity and low symmetry are difficult. The majority of the absorption bands in the 3300 cm^{-1} region have been identified and a number of frequencies in the $2000\text{--}600\text{ cm}^{-1}$ region characteristic of the fundamental vibrations have also been observed.^{1–4} The objective of this investigation is to identify the vibrational frequencies corresponding to each substituent, whether they are stretching vibrations associated bending vibrations.

EXPERIMENTAL

2,4-Dinitrophenylhydrazine (2,4-DNP) was prepared using a standard method. 5 Gms of purified 2,4-dinitrochlorobenzene is dissolved in 13 mL of warm ethylene glycol. The contents are cooled to a temperature of $15\text{--}18^\circ\text{C}$ by stirring and placed in an ice bath. 2–2.5 mL of hydrazine solution is added with the help of dropping funnel. When the reaction is over, the contents are digested with methanol. Now, the contents are cooled, filtered and washed with a little methyl alcohol. Finally, it is dried at about 100°C .

The infrared spectrum was measured in the range $4000\text{--}400\text{ cm}^{-1}$ on SPECORD-CARL SIZE75IR infrared spectrophotometer at Forensic Science Department, Madras. The vibrational band assignments observed in the spectrum is summarized in the Table 1.

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TABLE 1
 ASSIGNMENTS OF THE VIBRATIONAL FREQUENCIES OF 2,4-DINITROPHENYL
 HYDRAZINE

Frequency (cm ⁻¹)	Intensity	Assignments
3860	m	2906 + 968 = 3874
3753	m	3211 + 552 = 3763
3540	m	N-H Assym stretching
3513	m	N-H Sym stretching
3294	s	N-H stretching
3211	m-s	2 × 1600 = 3200
3040	m	C-H Aromatic Stretching
2906	m	C-H Aromatic Stretching
2813	m	C-H Aromatic Stretching
2632	m	3540 - 911 = 2629
2313	m	3513 - 1210 = 2303
2094	w	3294 - 1210 = 2084
2027	w	1400 + 611
1926	w	2906 - 968 = 1938
1779	w	2 × 611 + 552 = 177
1610	m	NH ₂ in-plane bending (scissoring)
1600	m	C-C ring stretching
1558	m	NO ₂ Assym stretching
1538	m	NO ₂ Assym stretching
1478	m	C-C ring stretching
1400	m	C-C ring stretching
1365	m	NO ₂ sym. stretching
1311	s	NO ₂ sym. stretching
1278	s	C-H in-plane bending
1270	s	C-H in-plane bending
1210	m	C-N stretching
1048	m	1600 - 552 = 1048
968	m	NH ₂ out-of-plane bending (wagging)
911	m	C-H stretching
697	m	C-H out-of-plane bending
611	m	C-C in-plane bending
552	m	C-C out-of-plane bending

s-Strong, m-s Medium to Strong, w-Weak.

RESULTS AND DISCUSSIONS

In previous works¹⁻⁴, it was shown that the presence of hydrogen bonding in certain pyridine derivatives could be clearly detected by infrared spectroscopy. Studies on previous works show that they may be extended to detect the

vibrational frequencies corresponding to each substituent of substituted pyridines. Ring vibrations of pyridine parallel to the benzene can be readily located and the C-H vibrations of pyridine show considerable divergence from those of benzene^{5,6}.

The aromaticity and the configuration of 2,4-DNP indicate that it belongs to C_s symmetry. Considering the compound, the derivative of nitro aniline, 2,4-dinitrophenylhydrazine on one hand and a substituted benzene on the other, the fundamental frequencies in the spectrum of the compound can be discussed as follows:

Aromatic Vibrations

Most mononuclear and polynuclear aromatic compounds have three or four peaks in the region 3080–3010 cm^{-1} due to stretching vibrations of the ring C-H bonds. The frequencies 3040 cm^{-1} and 2906 cm^{-1} in infrared spectrum have been assigned to aromatic C-H stretching vibrations. A number of C-H in-plane deformation bands occur in the region 1290–1000 cm^{-1} . The bands are usually sharp but of weak-to-medium intensity. The frequencies of the C-H out-of-plane deformation vibrations are mainly determined by the number of adjacent hydrogen atoms on the ring and not very much affected by the substituent⁷ although strong electron-attracting substituent groups can result in an increase of about 30 cm^{-1} in the frequency of the vibration. These bands give an important means for determining the type of aromatic substitution. The frequencies at 1278 cm^{-1} and 1270 cm^{-1} and at 697 cm^{-1} have been assigned to C-H in-plane bending vibrations and C-H out-of-plane bending vibrations respectively.

The ring C-C stretching vibrations^{8,9} occur in the region 1625–1530 cm^{-1} . For aromatic six-membered rings, there are two or three bands in this region due to skeletal vibrations, the strongest usually being about 1500 cm^{-1} . In general, mono-*meta*-di and 1,3,5 trisubstituted benzenes have strong bands at 1625–1590 cm^{-1} . Three bands observed at 1600 cm^{-1} , 1478 cm^{-1} and 1400 cm^{-1} have been assigned to aromatic ring carbon vibrations. These bands overlapped in the region of NO_2 stretching vibrations. Hence, these bands are carefully assigned and presented in the Table 1. For mono-substituted aromatics, bands due to out-of-plane deformations occur in the region 550–410 cm^{-1} . Hence the bands observed at 552 cm^{-1} and 611 cm^{-1} are due to out-of-plane carbon bending vibrations and in-plane carbon bending vibrations respectively.

Aliphatic Vibrations

Nitro compounds, nitrates and nitroamines contain NO_2 group. The exact position of the bands is dependent on substitution and unsaturation in the vicinity of the NO_2 group¹⁰. The frequencies observed at 1558 cm^{-1} and 1538 cm^{-1} have been assigned to NO_2 group asymmetrical stretching vibrations. The band observed at 1311 cm^{-1} and 1365 cm^{-1} have been assigned to NO_2 group symmetrical stretching vibrations. The medium-to-weak absorption bands for the C-N linkages in amines appear in the regions of 1200–1020 cm^{-1} ¹⁰. The characteristic strong bands which appeared at around 1250 cm^{-1} have been assigned to C-N stretching vibration. Further band due to N-H symmetric

stretching mode is observed at around 3400 cm^{-1} and band due to N-H asymmetric stretching mode is observed at around 3500 cm^{-1} . In addition to that, N-H bending vibrations are observed at around 1620 cm^{-1} . The remaining bands in the spectrum may be due to overtones and combinations of fundamentals.

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