

Electronic and vibrational spectra of 3,6-dichloro-pyridazine

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Abstract. The vibrational analysis and assignment of the infrared bands of 3,6-dichloro-pyridazine recorded in the region (300-4000 cm^{-1}) in KBr phase and electronic absorption band in the region (3625-3220 Å) in vapour phase are reported.

Keywords. Electronic spectra; vibrational spectra; dichloro-pyridazine.

1. Introduction

The sharp π^*-n spectra of azabenzenes generally permit their detailed vibrational and rotational analysis. Amongst the different diazines, the 3700 Å system of pyridazine presents a complex vibrational structure. Despite this complexity, vibrational analysis of this system was proposed by Tincher (1960). The rotational analysis proposed by Innes *et al* (1970) shows that the 3700 Å system is due to the transition ${}^1B_1-{}^1A_1$. Studies on the vibrational spectra of a few deuterated pyridazines are available in literature (Stidham and Tucci 1967), but the effect of substitution on the π^*-n system does not appear to have been studied. The present work on 3,6-dichloropyridazine is an attempt to fill this gap. In this study the electronic transition has been classified and a vibrational analysis to the band system is proposed.

2. Experimental details and results

Pure chemicals obtained from Fluka AG, Switzerland, were used without any further purification. The electronic absorption spectrum photographed on a Hilger medium quartz spectrograph using different path lengths is shown in figure 1. The bands in general appear sharp upto $\pm 5 \text{ cm}^{-1}$ and in the broad and diffuse bands upto $\pm 10 \text{ cm}^{-1}$. The position of the bands, their separation from 0,0 band and their assignments are presented in table 1. The infrared absorption spectra (shown in figure 2) recorded on a Perkin Elmer Spectrophotometer in KBr phase were calibrated using an error graph. The bands in the region

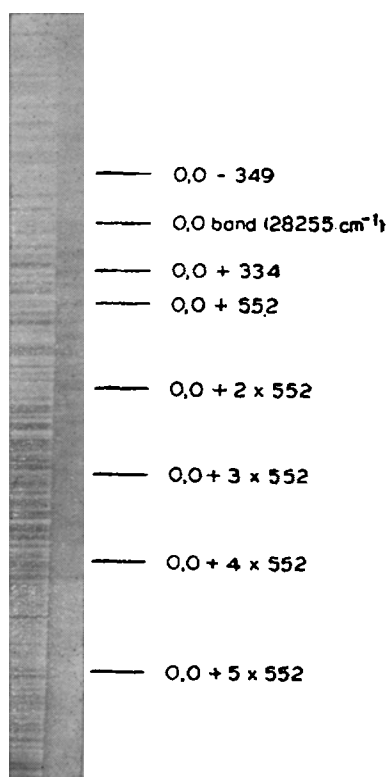


Figure 1. Near ultraviolet absorption spectra of 3,6-dichloro-pyridazine.

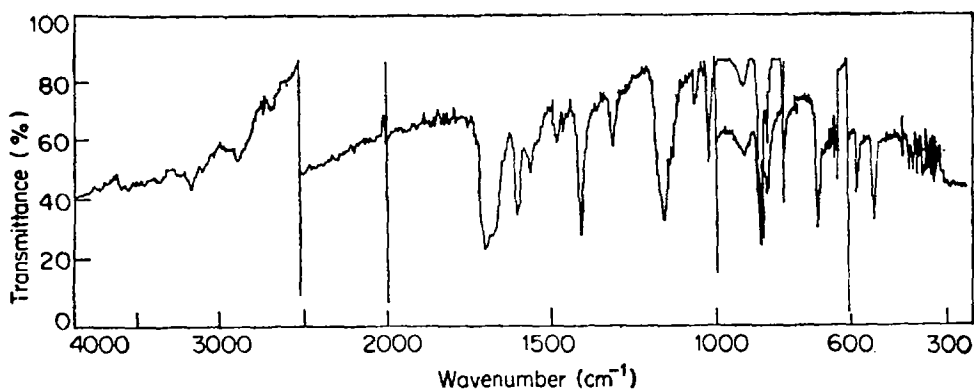


Figure 2. Infrared absorption spectra of 3,6-dichloro-pyridazine.

300–2000 cm^{-1} are correct upto $\pm 10 \text{ cm}^{-1}$ and in the region 2000–4000 cm^{-1} upto $\pm 20 \text{ cm}^{-1}$. The proposed analysis and assignment of these bands are presented in table 2.

Table 1. Analysis of the $n^*-\pi$ transition of 3,6-dichloro-pyridazine in near ultra-violet region.

Intensity	Position of the bands (A)	Position of the bands (cm^{-1})	Separation from 0,0 band (cm^{-1})	Assignment
w	3628.3	27553	0 - 702	0 - 2 \times 349
w	3613.2	27668	0 - 587	0 - 239 - 349
w	3597.7	27788	0 - 467	0 - 349 - 127
m	3582.4	27906	0 - 349	0 - 349
m	3568.3	28016	0 - 239	0 - 239
mb	3554.1	28128	0 - 127	0 - 127
ms	3538.2	28255	0 - 0	0,0 band
mb	3524.8	28362	0 + 107	0 + 107
ms	3512.4	28462	0 + 207	0 + 334 - 127
ms	3496.8	28589	0 + 334	0 + 334
ms	3485.3	28684	0 + 429	0 + 552 - 127
s	3470.4	28807	0 + 552	0 + 552
m	3456.3	28924	0 + 669	0 + 552 + 107
msd	3444.4	29024	0 + 769	0 + 552 + 334 - 127
ms	3430.6	29141	0 + 886	0 + 334 + 552
msb	3419.6	29235	0 + 980	0 + 2 \times 552 - 127
msd	3404.6	29364	0 + 1109	0 + 2 \times 552
msd	3392.7	29467	0 + 1212	0 + 2 \times 552 + 107
msd	3380.3	29575	0 + 1320	0 + 2 \times 552 + 334 - 127
mb	3365.9	29701	0 + 1446	0 + 2 \times 552 + 334
mb	3355.9	29790	0 + 1535	0 + 3 \times 552 - 127
msb	3341.7	29916	0 + 1661	0 + 3 \times 552
mb	3329.6	30025	0 + 1770	0 + 3 \times 552 + 107
mb	3318.5	30125	0 + 1870	0 + 3 \times 552 + 334 - 127
mb	3305.2	30247	0 + 1992	0 + 3 \times 552 + 334
wb	3294.5	30345	0 + 2090	0 + 4 \times 552 - 127
mb	3282.0	30460	0 + 2205	0 + 4 \times 552
wb	3269.7	30575	0 + 2320	0 + 4 \times 552 + 107
wb	3258.5	30680	0 + 2425	0 + 4 \times 552 + 334 - 127
wb	3245.2	30806	0 + 2551	0 + 4 \times 552 + 334
wb	3236.9	30885	0 + 2630	0 + 5 \times 552 - 127
wb	3223.0	31018	0 + 2763	0 + 5 \times 552

s = strong, msd = medium strong and diffuse, msb = medium strong and broad, ms = medium strong, m = medium, mb = medium and broad, w = weak, wb = weak and broad.

3. Discussion

In view of the structure, the C_{2v} point group has been assigned as pyridazine molecule by Innes *et al* (1970). The symmetry is maintained even after substituting the two chlorine atoms at 3 and 6 positions in the pyridazine ring and therefore

Table 2. Infrared absorption spectrum and assignments for 3,6-dichloro-pyridazine

Position of the bands in cm^{-1} along with their intensities*	Assignment	Position of the bands in cm^{-1} along with their intensities*	Assignment
344 (ms)	γ (C-Cl)	1394 (vs)	ν_{10a}
354 (ms)	γ (C-Cl)	1412 (w)	1010 + 402
358 (ms)	β (C-Cl)	1430 (vw)	644 + 784
376 (ms)	β (C-Cl)	1448 (m)	622 + 834
402 (ms)	ν_{16a}	1464 (ms)	ν_{19b}
508 (vs)	ν_{16b}	1472 (sh)	784 + 682
564 (vs)	ν_{6a}	1486 (vw)	644 + 844
622 (vs)	ν (C-Cl)	1522 (w)	682 + 844
644 (m)	ν_{6b}	1530 (w)	682 + 852
682 (vs)	ν (C-Cl)	1548 (ms)	ν_{8a}
738 (w)	ν_4	1586 (s)	ν_{8b}
784 (vs)	ν_{11}	1676 (vsb)	2×844
834 (vs)	ν_{30}	1730 (vw)	1394 + 334
844 (vs)	ν_{10}	1770 (vw)	1394 + 376
852 (vs)	ν_1	1784 (vw)	644 + 1148
1010 (vs)	ν_{18}	1808 (vw)	1464 + 344
1046 (m)	644 + 402	1834 (w)	682 + 1148
1078 (vw)	738 + 344	1842 (vw)	1010 + 834
1090 (vw)	738 + 354	1980 (w)	834 + 1148
1118 (ms)	738 + 376	2076 (vw)	784 + 1294
1130 (ms)	784 + 344	2100 (vw)	644 + 1464
1148 (vs)	ν_9	2122 (vw)	834 + 1294
1264 (vw)	622 + 644	2156 (vw)	1010 + 1148
1280 (vw)	2×644	2176 (vw)	784 + 1394
1294 (s)	ν_{14}	2224 (vw)	834 + 1394
1322 (vw)	644 + 682	2764 (w)	1294 + 1464
1344 (vw)	564 + 784	2996 (w)	1464 + 1548
1352 (vw)	1010 + 344	3050 (sh)	ν_7
1360 (vw)	622 + 738	3070 (w)	ν_8
		3134 (ms)	1548 + 1586

vs = very strong, s = strong, ms = medium strong, m = medium, w = weak, vw = very weak, sh = shoulder

* Intensities are shown in parentheses against each wave-number.

the electronic band system of 3,6-dichloro-pyridazine appears due to the ${}^1B_1 - {}^1A_1$ transition. The strongest band at 28255 cm^{-1} towards the longer wavelength of the spectrum, has been classified as the 0,0 band. Strong bands at 28589 and 28807 cm^{-1} towards the shorter wavelength involves a separation of 334 and 552 cm^{-1} from the 0,0 band. These separations have been taken as the fundamental vibrational frequencies at the excited state. Hot bands at 28016 and 27906 cm^{-1}

towards the longer wavelength of the 0,0 band involves two (239 and 349 cm^{-1}) fundamental vibrational frequencies in the ground state. The fundamental vibrations of a few important ones are discussed below.

3.1. Ring vibrations

Spectroscopic investigations on the spectra of benzene show that the ν_1 vibration (995 cm^{-1}) represents the carbon stretching vibration (breathing type). The UV, IR and Raman spectra of substituted benzenes also show that this vibration is mass-dependent and has been assigned upto 700 cm^{-1} (Padhye and Viladkar 1959; Whiffen and Stojiljkovic 1958; Wilmshurst and Bernstein 1957) depending upon the mass and nature of the substituent. In the case of pyridazine, a very strong infrared band at 963 cm^{-1} and polarised Raman band at 964 cm^{-1} has been assigned to this mode by Stidham and Tucci (1967). Studies on the vibrational spectra of pyridazine 3,6 d_2 and pyridazine d_4 by these authors also indicate that this vibration is mass-dependent. In our electronic spectrum there is a strong band at 28807 cm^{-1} towards the shorter wavelength of the 0,0 band. This involves an excited state fundamental frequency at 552 cm^{-1} . This vibration has been traced upto five quanta. The major part of the spectrum has been explained by the combinations and overtones of this vibration. The corresponding ground state vibration has not been identified since the system does not extend much towards the longer wavelength. However, a strong infrared band at 852 cm^{-1} has been taken to represent the ground state vibration which has been taken as the ring stretching vibration (breathing type), analogous to the ν_1 mode of benzene.

In the infrared absorption spectra, a pair of bands (1394 and 1464 cm^{-1}) and (1548 and 1586 cm^{-1}) appearing with sufficient intensity is assigned as the components of ν_{19} and ν_8 vibrations respectively. This agrees with the assignments made earlier for pyridazine (Stidham and Tucci 1967) and disubstituted benzenes (Padhye and Viladkar 1959; Whiffen and Stojiljkovic 1958; Wilmshurst and Bernstein 1957; Bellamy 1959).

In the spectra of benzene, ν_6 represents a carbon planar deformation vibration of e_2 type. Under the C_{2v} point group the degeneracy is removed and the two vibrations appear separately. Studies on the infrared spectra of pyridazine and some of its deuterated compounds show that the lower component is mass-dependent while the higher one remains around 650 cm^{-1} . In the present electronic spectrum there is a medium strong fundamental at 334 cm^{-1} in the excited state. Higher quanta of this vibration has not been identified but a large number of combinations are observed. A strong infrared band at 564 cm^{-1} has been taken to represent its ground state value. This vibration has been assigned as a_1 component of ν_6 vibration. The b_2 component due to its weak intensity could not be identified in both the states. A similar type of large reduction of ν_{6a} component has been observed in pyridazine d_4 by Innes *et al* (1970).

Under reduced symmetry, the degenerate vibration ν_{16} (e_{2g} , 404 cm^{-1}) splits into its components. Job and Kartha (1977) have assigned one of the components of ν_{16} upto 488 cm^{-1} in substituted pyridimines. In view of this the strong band observed at 508 cm^{-1} has been assigned to this mode. The other component of ν_{16} has been identified at 402 cm^{-1} in the present case. These assignments also find support from the work of Green and Harrison (1976).

3.2. Other vibrations

The molecule in the present study is a disubstituted pyridazine, i.e. there are only two hydrogen atoms attached with the ring. These two atoms will involve two C-H stretching, two C-H planar and two C-H non-planar bending vibrations. The position of these vibrations is not sensitive to the substituent. On the basis of data available for pyridazine and N-heterocyclic molecules (Bellamy 1959; Goel *et al* 1976; Sanyal *et al* 1977), these vibrations are assigned and presented in table 2.

It has been suggested by Bellamy (1959), that C-Cl stretching vibration lies in the frequency range (600–800 cm^{-1}). On the basis of data available for chlorinated aromatics (Anno and Matubra 1955, 1956; Deb *et al* 1960; Sponer and Kirby-Smith 1941), the symmetric and asymmetric stretching and planar and non-planar bending vibrations pertaining to the C-Cl bond are assigned and listed in table 2.

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References

- Anno T and Matubra I 1955 *J. Chem. Phys.* **23** 796
Anno T and Matubra I 1956 *J. Chem. Phys.* **24** 595
Bellamy L J 1959 *Infrared spectra of complex molecules* (New York: John Wiley)
Deb K K and Banerjee S B 1960 *Indian J. Phys.* **34** 554
Goel R K, Sanyal Nitish K and Srivastava S L 1976 *Indian J. Pure Appl. Phys.* **14** 842
Green J H S and Harrison D J 1976 *Spectrochim Acta* **A32** 1265
Innes K K, Tincher W C and Pearson E F 1970 *J. Mol. Spectrosc.* **36** 114
Job V A and Kartha S B 1977 *Proc. Indian Acad. Sci.* **A85** 476
Padhye M R and Viladkar B G 1959 *J. Sci. Ind. Res.* **B18** 504
Sanyal Nitish K, Srivastava S L and Goel R K 1977 *Indian J. Phys.* **B51** 108
Sponer H and Kirby-Smith J S 1941 *J. Chem. Phys.* **9** 667
Stidham H D and Tucci J V 1967 *Spectrochim Acta* **A23** 2233
Tincher W C 1960 Ph.D. Thesis, Venderbilt University
Whiffen D N and Stojiljkovic A 1958 *Spectrochim Acta* **A12** 42
Whilmshurst J K and Bernstein H J 1957 *Can. J. Chem.* **35** 911