Asian Journal of Chemistry Vol. 10. No. 3 (1998), 527–531

Infrared Spectra of 2-Amino-4,6-Dichloro Pyrimidine

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The IR spectra of 2-amino-4,6-dichloropyrimidine have been recorded on Perkin-Elmer spectrophotometer in the region 4000–200 cm^{-1} using KBr-pellet technique. The spctrum has been analysed assuming C_{2v} point group symmetry for the molecule. The probable assignments to the obeserved fundamental frequency with structural features have been assigned to different modes of vibrations on the basis of magnitude and relative intensity of the recorded spectra and group frequency approach with analogy to the similar molecules.

INTRODUCTION

The N-heterocyclic molecules such as pyrimidine, pyridine, cytosin, thyamin and their derivatives are of great biological importance as they play a central role in structure and properties of nucleic acids. However due to of their high complexity and low symmetry, the interpretation of the spectra is difficult. However in view of the chemotherapeutic importance of substituted pyrimidines, a detailed study of their vibrational and electronic spectra is relevant. Many spectroscopists have reported the vibrational spectra of pyrimidne ring compounds.[1–8] In continuation of our studies of substituted pyrimidines,[9] the present paper reports the infrared spectra of 2-amino-4,6-dichloropyrimidine, which has not been done so far. The interpretation of the observed bands is based on our present study, mainly on the group frequency approach and on the analogy between the spectra of molecules of similar structure.

EXPERIMENTAL

The spec-pure chemical 2-amino-4,6-dichloropyrimidine (2,4,6-ADCP) was obtained from Sigma-Aldrich (U.S.A.) and used as such without further purificatin. However, its purity was confirmed by elemental analysis and m.p. determination. The IR spectra for this compound was recorded on Perkin-Elmer spectrophotometer using KBr pellet technique in the region 4000–200 cm^{-1}.

RESULTS AND DISCUSSION

The structures of several pyrimidine compounds have been determined by Lancaster and Stoicheff[10] and Wheatley[11] and in all cases the molecules were found to be planar. The observed ring fundamentals are given in Table-1. The group frequencies are given in Table-2 along with their correlation with similar molecules. All the fundamentals have been described in the form of Wilson notations and have also been compared with the mode of pyrimidine-d_2[12] shown in Table-1. From the point of view of the position of substituents and by assuming NH_2 as a single mass point the present molecule of 2,4,6-ADCP would belong to C_{2v} point group symmetry.

TABLE-1

ANALYSIS OF THE IR ABSORPTION SPECTRA (cm^{-1}) OF 2, 4, 6-ADCP AND CORRELATION OF FUNDAMENTALS WITH THOSE OF PYRIMIDINE

Vibration No.	Pyrimidine frequency (cm^{-1}) (Ref. 7)	2-Amino-4,6-dichloro pyrimidine (frequency with intensity cm^{-1})	Assignments	
17a	1870	220 m	C—Cl	o.p.b.
18b	1071	300 s	C—Cl	i.p.b.
16b	344	340 s	C—C	o.p.b.
9a	1137	400 ms	C—Cl	i.p.b.
6a	678	510 vvw	C—C—	i.pb.
13	3038	550 s	C—Cl	stretching
7b	3086	610 vs	C—Cl	stretching
6b	623	620 m	C—C—	i.p.b.
4	708	690 vvw	C—C—	o.p.b.
1	992	795 vs	C—H	stretching ring breathing
11	811	845 w	C—C—	o.p.b.
12	1065	925 vs	C—H	i.p.b.
		1010 s		NH_2 twisting
3	1225	1160 vs	C—H	i.p.b.
2	3052	1305 vvs	C—NH_2	stretching
19a	1398	1370 m	CC—CN	stretching
19b	1466	1430 ms	CC—CN	stretching
8a	1564	1540 vvw	CC—CN	stretching
8b	1568	1635 vvw	CC—CN	stretching
		1650 vvw	NH_2	scissoring
20a	3074	3100 s	CH	stretching
		3200 vw	N—H	stretching
		3390 ms	N—H	symm. stret.
		3470 vs	N—H	Asymm. stret.

s = strong, Vs = Very strong, VVs = Very-very strong, ms = medium strong,
m = medium, w = weak, VW = very weak, VVW = very-very weak.
i.p.b. = in-plane bending, o.p.b. = out-of-plane bending,, Symm = Symmetric,
Asymm = Asymmetric

TABLE-2
COMPARISON OF AMINO GROUP FREQUENCY WITH SIMILAR MOLECULES
(All values in cm^{-1})

Assignments	2,4,6-ADCP (Present molecules)	2,4,6-Triamino-pyrimidine (Ref. 16)	4-Amino-2, 6-Dihydroxy Pyrimidine (Ref. 8)
$\nu_{asym}(NH)$	3470	3430	3400
$\nu_{sym}(NH)$	3390	3319	3300
NH_2 Scissoring	1650	1642	—
NH_2 Twisting	1010	1094	1060

C—H Vibrations: In pyrimidine there are three C—H stretching modes belonging to the a_1 species and one belonging to the b_2 species. On substitution at 4 and 6 positions, the modes ν_{13} and ν_{7b} drop in accordance with the assignments given by Nejad and Stidham[12] for pyrimidine-4, 6-d_2; the modes ν_{13} and ν_{7b} drop when substitutions are made at 4 and 6 positions. Since the molecule is penta-substituted, only one C—H stretching vibration is expected, which lies in the region 3100–3000 cm^{-1} as suggested by Bellamy.[13] Thus in the present case the band observed at 3100 cm^{-1} has been assigned to C—H stretching mode ν_{20a}. Similarly a band observed at 1160 cm^{-1} has been assigned to ν_3 vibration mode corresponding to C—H in-plane bending mode. The C—H out-of-plane bending mode ν_{11} has been assigned at 829 cm^{-1}.These above values find support from the work of Goel *et al.*[14] in case of some N-heterocylic molecules and other workers.[15–17]

C—C and C—N Vibrations: In the spectra of pyrimidine[12] pairs of absorption bands at 1398 (ν_{19a}), 1466 (ν_{19b}) cm^{-1} and at 1564 (ν_{8a}), 1568 (ν_{8b}) cm^{-1} have been observed which are analogous to the pair of bands originating from e_{1u} (1485) and e_{2g} (1595) modes of benzene, observed in substituted benzenes.[13] In the present study, these bands ν_{19a}, ν_{19b}, ν_{8a}, ν_{8b}, thus have been assigned at 1398, 1466, 1564, 1568 cm^{-1} respectively, which are in analogy with the study given by previous workers.[18–20]

In substituted benzenes, the frequency of one of the ring modes ν_1 and ν_{12} reduces to *ca.* 820 cm^{-1} while the other remains at *ca.* 1000 cm^{-1}. In view of these assignments, the bands at 795 and 925 cm^{-1} in the present molecule 2,4,6-ADCP have been assigned to correspond to ν_1 and ν_{12} modes respectively and find support.[21–24]

The ring out-of-plane bending vibrations ν_4, ν_{16a} and ν_{16b} in pyrimidine[12] appear at 708, 399 and 344 cm^{-1} respectively. The bands observed at 690 and 340 cm^{-1} in the present case of 2,4,6-ADCP have been assigned to ν_4, ν_{16b} modes respectively. These also find support from the work of Goel *et al.*[14] and Kartha *et al.*[15] in substituted pyrimidines. The ring planar deformations ν_{6a} and ν_{6b} in 5-methylpyrimidine[15] were assigned at 559 and 639 cm^{-1} respectively. In the present molecule these modes are identitied at 620 to 510 cm^{-1} respectively. This is also in agreement with the assignments of previous workers.[25–27]

Group vibrations

(a) *Amino group vibrations*: In most of the primary aromatic amines, there occur two bands in the region 3550–3350 cm^{-1} which are associated with N—H stretching vibrations. It has been pointed out by Bellamy[13] that in N-octamide in chloroform solution, the NH_2 free absorption occurs at 3415 and 3530 cm^{-1} but it also shows additional bands at 3498, 3345, 3300 and 3182 cm^{-1}. This suggests the occurrence of different types of simultaneous associations of free and banded N—H bonds. In solid states the pattern simplifies and gives two broader NH peaks near 3350 cm^{-1} and 3164 cm^{-1}. In view of these assignments, we have assigned the bands observed at 3200, 3390 and 3470 cm^{-1} to N—H stretching. symmetric and asymmetric modes respectively. These are also in accordance with the empirical relationship of Bellamy and Williams,[28] $\nu_{sym} = 345.03 + 0.876\ \nu_{asym}$. The NH_2 scissoring mode has been suggested to lie in the region 1650–1590 cm^{-1}.[13, 29] The NH_2 scissoring mode has been identified at 1650 cm^{-1} in the present case. The NH_2-twisting frequency[30] lies around 1060 cm^{-1}. Thus this mode has been found at 1010 cm^{-1} in the present case. The NH_2 stretching mode has also been identified at 1305 cm^{-1} in accordance to literature.[31]

(b) *Cl-group vibrations*: Previous workers[32, 33] observed the C—Cl stretching modes in the region 650–550 cm^{-1}. The infrared bands observed at 610 cm^{-1} have been assigned as the C—Cl stretching modes in the 2,4,6-ADCP molecules; these find support from literature values.[14, 34] Green *et al.*[35] assigned the C—Cl out-of-plane bending mode in the region 200–110 cm^{-1} in the vibrational spectra of various chloro-substituted benzenes. In view of this a band observed at 220 cm^{-1} in the spectra of the present molecule has been assigned to the above mode. The C—Cl in-plane bending modes have been identified at 400 and 300 cm^{-1} in accordance with the previous works.[8, 9, 36]

REFERENCES

1. M. Ito, R. Shimada, T. Kuraishi and W. Muzushima, *J. Chem. Phys.*, **25**, 596 (1956).
2. R.C. Lord, A.J. Masson and F.A. Miller, *Spectrochim. Acta*, **9**, 113 (1957).
3. J.D. Simmons and K.K. Innes, *J. Mol. Spectrosc.*, **13**, 435 (1964).
4. G. Sbrana, G. Adembri and S. Califano, *Spectrochim. Acta*, **2**, 1831 (1966).
5. Y.A. Sharma, *Spectrochim. Acta.*, **30A**, 1801 (1974).
6. M.T. El-Haty, A.E. Mohamed, F.A. Adam and A.A. Gabr, *Spectrochim. Acta*, **46A**, 1743 (1990).
7. S. Mohan and V. Ilangovan, *Indian J. Pure and App. Phys.*, **32**, 256 (1994).
8. Vibha Sharma, S.D. Sharma and V.K. Sharma, *Asian J. Chem.*, **7**, 855, (1995).
9. Praveen Kumar and S.D. Sharma, *Asian J. Chem.*, **8**, 792 (1996).
10. J.E. Lancaster and B.P. Stoicheff, *Can. J. Phys.*, **34**, 1016 (1956).
11. Wheatley, *Acta Crystallogr*, **13**, 80 (1960).
12. Nejad and Stidham, *Spectrochim, Acta*, **31**, 1433 (1975).
13. L.J. Bellamy, The IR Spectra of Complex Molecules, Chapman and Hall, London (1975).
14. R.K. Goel, N.K. Sanyal and S.L. Srivastava, *Indian J. Pure. and Appl. Phys.*, **14**, 842 (1976).
15. V.A. Job and S.B. Kartha, *Proc. Indian Acad. Sci.*, **85A**, 476 (1977).
16. R.K. Goel, N.K. Sanyal and S.N. Sharma, *Indian J. Phys.*, **53B**, 282 (1979).

17. R.K. Goel, *Spectrochim. Acta*, **40A**, 723 (1984).
18. R.K. Goel and S.N. Sharma, *Indian J. Pure and Appl. Phys.*,**18**, 195 (1980).
19. R.K. Goel and Salik Ahmed, *Indian J. Phys.*, **59B**, 488 (1985).
20. P. Carmona, M. Molina and R. Escobar, *Spectrochim. Acta*, **49** (1993).
21. A. Kwal and K. Machida, *Spectrochim. Acta*, **35A**, 27 (1979).
22. G.T. Towans, *Spectrochim. Acta*, **39A**, 801 (1983).
23. N.D. Patel, S.B. Kartha and N.A. Narsimham, *J. Mol. Spectrosc.*, **48**, 185 (1973).
24. S.B. Kartha, *Can. J. Spectrosc.*, **27**, 1 (1982).
25. Praveen Kumar and S.D. Sharma, *Acta Ciencia Indica.*, 3034-P (1996).
26. J.K. Wiliamshurst and H.J. Bernstine, *Canad. J. Chem.*, **35**, 911 (1975).
27. R.K. Goel and (Km) C. Gupta, *J. Raman Spectrosc.*, **16**, 1 (1985).
28. L.J. Bellamy and R.L. Williams, *Spectrochim. Acta*, **9**, 341 (1957).
29. C.N.R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York (1963).
30. J.C. Evans, *Spectrochim. Acta*, **16**, 428 (1960).
31. N.K. Sanyal, S.L Srivastava and R.K. Goel, *Indian J. Phys.*, **51B**, 108 (1977).
32. S.N. Singh and N.L. Singh, *Indian J. Pure and Appl. Phys.*, **7**, 250 (1969).
33. N.K. Sanyal, S.L. Srivastava and R.K. Goel, *Indian J. Pure and Appl. Phys.*,**16**, 719 (1978).
34. G.N.R. Tripathi and S. Ram, *Indian J. Pure and Appl. Phys.*, **12**, 529 (1974).
35. J.H.S. Green, D.J.. Harrison and C.P. Stockley, *Spectrochim. Acta.*, **33A**, 423 (1977).
36. S.N. Sharma and C.P.D. Dwivedi, *Indian J. Phys.*, **50**, 25 (1976).

(*Received:* 8 December 1997; *Accepted:* 2 February 1998) AJC- 1432