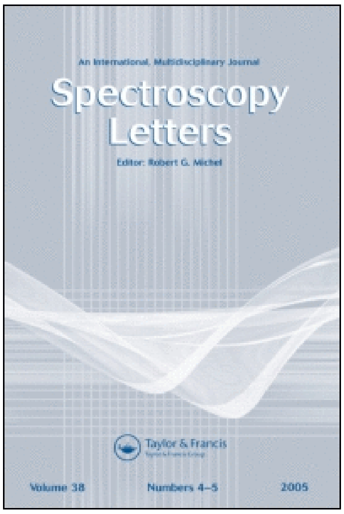


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

The Vibrational Spectra of Organic Ligands. Part I. 2-Acetylpyrrole

J. C. Viljoen[a]; A. M. Heyns[a]
[a] Chemistry Department, University of Pretoria, Pretoria, South Africa

To cite this Article Viljoen, J. C. and Heyns, A. M.(1987) 'The Vibrational Spectra of Organic Ligands. Part I. 2-Acetylpyrrole', Spectroscopy Letters, 20: 10, 765 — 776
To link to this Article: DOI: 10.1080/00387018708081585
URL: http://dx.doi.org/10.1080/00387018708081585

SPECTROSCOPY LETTERS, 20(10), 765-776 (1987)

THE VIBRATIONAL SPECTRA OF ORGANIC LIGANDS. PART I. 2-ACETYLPYRROLE

KEY WORDS: Infrared, Raman, High-pressure, 2-acetylpyrrole, hydrogen bonding

J.C. Viljoen and A.M. Heyns
Chemistry Department, University of Pretoria, 0002
Pretoria, South Africa

ABSTRACT

The infrared and Raman spectra of 2-acetylpyrrole dissolved in various solvents, are reported in addition to the Raman spectra of the solid state at pressures up to 30 kbar. The high-pressure behaviour of the Raman-active N-H bands shows beyond any doubt that hydrogen bonded species exist in solid 2-acetylpyrrole, but these results could not distinguish between intra- or intermolecular bonds. Evidence of hydrogen bonded species was also found in solutions of 2-acetylpyrrole in addition to vibrations which point to the existence of 'free' or anti-bonded molecules. The hydrogen bonded species existing in solutions and in the solid state appear to be identical.

INTRODUCTION

The infrared spectra of pyrrole and its derivatives have been studied by several investigators[1-5], however, no complete infrared or Raman studies of 2-acetylpyrrole in particular have been reported in the literature. This compound is of interest as a bidentate ligand in a variety of inorganic complexes[6-8] and also because of the anti- and syn-conformations that it can adopt as well as inter- and intra-molecular hydrogen bonding that can occur between and within molecules in both the solid state and in solution. For these reasons we have undertaken a study of the vibrational spectra of this ligand. In the present paper we report the Raman spectra of 2-acetylpyrrole in the solid state under various pressures, in tetrachloromethane solution as well as the FT-IR spectra in various solvents.

EXPERIMENTAL

The 2-acetylpyrrole was obtained from Aldrich Chemical Company and used without further purification.

The Raman spectra (4000 to 60 cm^{-1}) were recorded on a Dilor Z24 Raman spectrometer equipped with a Coherent Radiation INNOVA-5 laser operating on the 514 nm line. A high pressure cell described elsewhere[9] was used to obtain spectra at various pressures up to approximately 30 kbar.

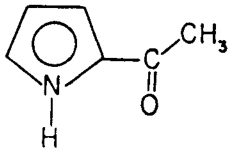
The infrared spectra were recorded with a Bruker IFS 113V Fourier transform infrared spectrometer between 4000 and 400 cm^{-1} with a Specac vacuumtight cell (type 1501), with a path length of 0,1 mm.

The spectral resolution was 4 cm^{-1} for the infrared spectra and 2 cm^{-1} for the Raman spectra.

RESULTS AND DISCUSSION

The results are summarized in Table 1. Because the frequencies obtained from the tetrachloroethylene solution are very similar to those of the CCl_4 solution, only the latter are given. As an example of the mid-infrared spectrum of the molecule, the spectrum of 2-acetylpyrrole in hexane is presented in Figure 1. All results are summarised in Table 1, including the pressure dependence ($d\nu/dP$-values) of some of the Raman spectra. 2-Acetylpyrrole dispersed in KBr did not give infrared spectra of an acceptable quality, and are therefore not included in Table 1.

The 2-acetylpyrrole molecule is shown below and the



highest symmetry that can be assigned to it is C_s. Be-

TABLE 1

Observed Infrared and Raman frequencies for 2-acetylpyrrole (350-4 000 cm^{-1})*

Infrared			Raman		
Solution Hexane	Solution CCl_4	Solution CH_2Cl_2	Solution CCl_4	Solid	$d\nu/dP$ $cm^{-1}/kbar$
				388w	0.71
511vw	511vw	505vw	502m	503m	
544vw	548vw	548m,br			
555vw	555vw	-			
580vw	584vw	590w			
606vw	606w	607m			
629vw	629w	625m	629vw	640vw	
677vw	677vw	679m			
739vw	735w	:			
766w	:	:		762vw	
814vw	:	:			
839vw	:	825w			
883vw	883w	883vw	881m	879m	0.14
			925s(p)	921s	
928w	928m	928s			0.43
972vw	972w	970w	968w	968w	0.45
1022vw	1022vw	1022vw	1023w		
1043w	1043m	1041vs	1040m	1038m	0.32
1068vw	1068vw				
1074vw	1074vw	1070w	1075m(p)	1075m	0.34
1107vw	1109w	1111s			
1136w	1136vw	1136sh	1144s	1138m	0.61
	1142				
		1266	1266w		
		1298	1298vw		
1311vw	1315m	:			
1325vw	1323w	1319vs	1327w(dp)	1324w	
1360vw	1358w	1362m	1362m(dp)	1366m	0.26
1404s	1404vs	1406vs	1401s(dp)	1391s	0.41
1427w	1427s	1427sh	1428m	1425m	0.65
1454vs			1449m		
			1526w		
1549w	1549m	1547s	1554w		
1649vs	1645vs	1647vs,br	1638vs(p)	1628vs	0.08
1666sh	1655sh		1655sh		
			1699vvw		
			1910w(p)		
			2924m	2924w	1.08
				3127w	
			3136m	3113w	0.63
3286m,br	3286s,br	3286,br	3262w	3261w	-1.27
3464w	3458w	3442s,br	3433w		

*p - polarized, dp - depolarized, : solvent absorption

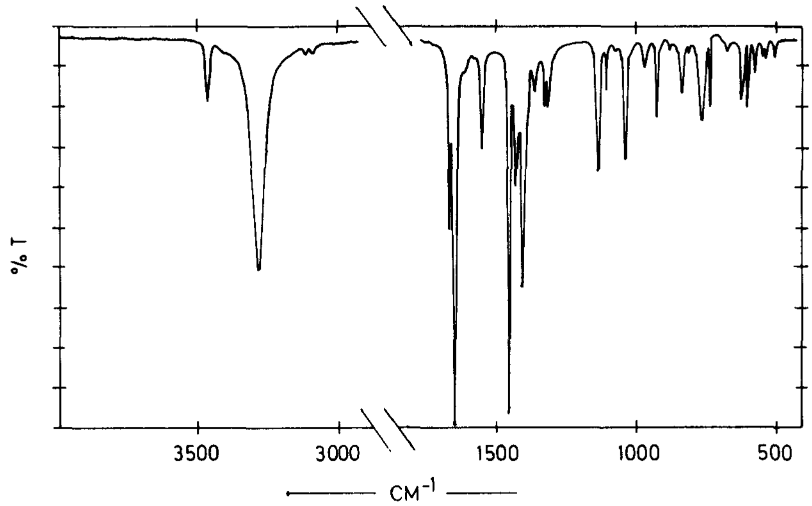


Fig. 1. The FT-IR spectrum of 2-acetylpyrrole dissolved in hexane.

cause of its low symmetry, all the vibrational modes are both infrared and Raman-active.

In an attempt to assign the observed Raman and infrared bands, the spectral results were compared with those of 2-methylpyrrole[3]. It is further evident that the vibrational bands cannot simply be viewed as stretching or bending modes, but that extensive coupling of modes will and do in fact occur. Therefore, instead of attempting to assign each individual band in the vibrational spectrum of 2-acetylpyrrole groups of bands are rather assigned, and the more important groups of vibrations which have been identified are summarized in Table 2.

TABLE 2
Assignments for 2-acetylpyrrole.

Frequency (cm^{-1})	Assignment
50 - 190	lattice modes
190 - 883	C-H and ring out-of-plane modes
928 - 1547	In-plane C-H, N-H and ring modes
1638 - 1649	νCO (hydrogen bonded)
1655 - 1699	νCO ('free')
2924	νCH (methyl groups)
3113 - 3136	νCH (ring)
3262 - 3286	νNH (hydrogen bonded)
3433 - 3464	νNH ('free')

As is shown in Table 2, the N-H band (not hydrogen bonded) occurs above 3430 cm^{-1}, whereas the N-H (hydrogen bonded) mode occurs at 3286-3262 cm^{-1}. In the Raman spectrum of solid 2-acetylpyrrole a broad and weak mode is observed at 3261 cm^{-1} which can be assigned to N-H hydrogen-bonded vibrations. Further evidence for hydrogen bonding is provided by the fact that this mode is the only one that shifts downwards upon an increase in the sample pressure ($d\nu/dP = -1.27$ cm^{-1}/kbar) as is shown in Fig. 2. This indicates that the O---H (hydrogen bond) strength is increased with pressure with a concomitant decrease in the N-H bond strength. A crystal structure determination of 2-benzoylpyrrole[10] has shown that it exists as hydrogen-bonded centrosymmetric dimers in the solid state. An analogous

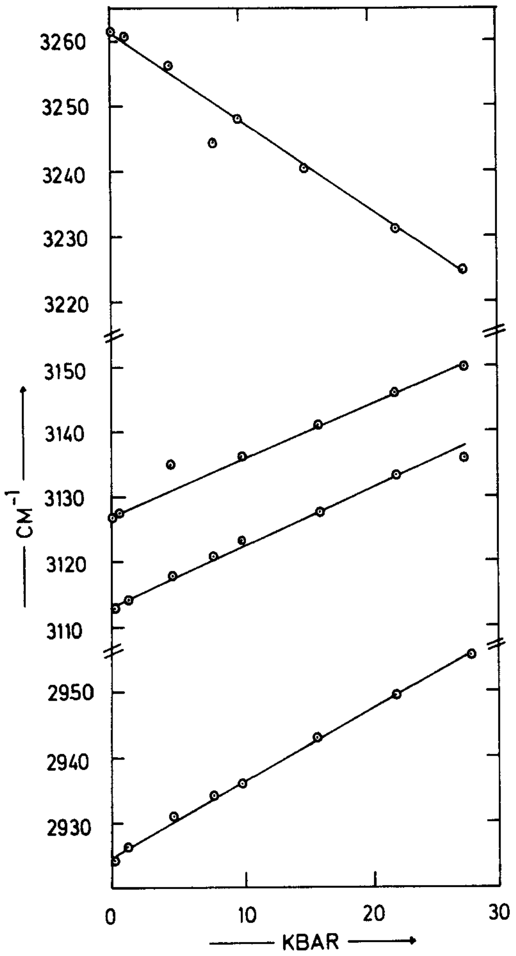
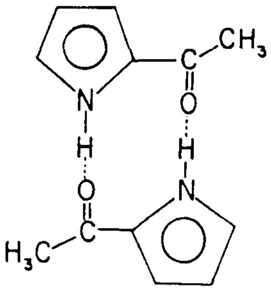
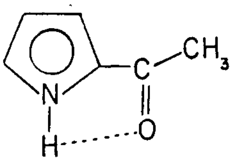


Fig. 2. The pressure dependence of the Raman-active N-H stretching mode (top), the C-H ring stretching modes (middle) and the C-H stretching mode of the methyl groups (bottom).

representation of a dimeric structure for 2-acetylpyrrole is shown below. In solution in both the infrared and Raman



spectra bands have been observed in the N-H hydrogen-bonded and non-hydrogen bonded frequency ranges. For example, in CCl_4 solution the infrared bands occur at 3286 and 3458 cm^{-1} and in the Raman spectra at 3262 and 3433 cm^{-1}. This shows that in solution a hydrogen-bonded and a free form are probably present (see later discussion of the C=O vibrations.) However, in the solid state only one mode was observed showing that hydrogen-bonded dimers most probably exist as in the case of the 2-benzoylpyrrole. The present spectroscopic results can, however, not distinguish between intramolecular (shown below) and intermolecular hydrogen-bonded



species since the frequency ranges where these N-H modes occur[11] in pyrroles both overlap with the ones where the N-H modes have been observed in 2-acetylpyrrole. Both of these hydrogen-bonded species are, however, known to exist in pyrroles[11].

The C-H ring modes have been observed in the Raman spectra in the frequency range where they can be expected to occur (Table 2). The C-H stretching modes of the methyl groups in 2-acetylpyrrole occur at 2924 cm^{-1} in the Raman spectra and are weak and broad showing no splitting. They are also rather pressure sensitive ($d\nu/dP = 1.08\ cm^{-1}/kbar$). In 2-methylpyrrole, the methyl groups do not rotate freely and three C-H bands are observed in the infrared spectrum[3]. One possible explanation for the behaviour of the C-H stretching bands in 2-acetylpyrrole is that the CH_3 groups have more rotational freedom than in 2-methylpyrrole thus causing the C-H bands to be broad and rather weakly defined in the Raman spectra. These modes were absent in the infrared spectra of solutions of 2-acetylpyrrole.

In both the infrared and Raman spectra of 2-acetylpyrrole (with the exception of the CH_2Cl_2 solutions) two features have been observed which can be assigned to C=O modes. In addition to the preferred syn conformation a 'free' anti form shown below, is probably also present in solution. The possibility of free rotation is excluded because the ring and the carbonyl moiety forms an extended delocalized system which can only exist if the C=O bond is in the same plane as the ring. The hydrogen-bonded conformation (either inter- or intramolecular) is probably present in greater abundance than the 'free' anti form. The more intense C=O band at ~1640 cm^{-1} can then be assigned to a hydrogen-bonded system while the higher-frequency shoulder represents a C=O mode of the 'free' system. In the most polar solvent, CH_2Cl_2, the C=O peak broadens and the shoulder disappears. In the solid state, only one C=O mode is observed in agreement with the previous conclusion that the molecules are probably hydrogen-bonded dimers. This C=O band is virtually unaffected by pressure and a possible explanation for this behaviour is that the normal increase in C=O bond strength with pressure is offset by an increase in the O---H bond strength. Kay et al.[11] concluded that no anti form exists in 2-acylpyrroles in solution but that various hydrogen-bonded conformations are present. However, the higher frequency N-H bands observed in 2-acetylpyrrole are so typical of a non-hydrogen bonded N-H group that this clearly indicates the existence of the anti-form in solution. This latter conformation is the only possible 'free' non-hydrogen bonded conformation of the 2-acetylpyrrole molecule. It was reported elsewhere that the hydrogen-bonded centrosymmetric dimers in 2-benzoylpyrrole which hold the molecules together are not observed in benzene solution[10]. However, in the solutions studied in the present work it appears that there is very little difference in the N-H frequencies observed in solution and in the solid state and it can thus be concluded that the same type of hydrogen-bonding exist in both solid and dissolved 2-acetylpyrrole.

The so-called ring breathing mode of pyrrole and its derivatives has been the subject of numerous arguments. For pyrrole the observed and calculated values are 1144 and 1159 cm^{-1} respectively and in the present results this mode was observed at 1136-1144 cm^{-1}. This mode is most probably not a pure breathing one, as it can be accompanied by in-plane bending C-H modes. In the Raman spectrum it was observed to be fairly pressure sensitive with $d\nu/dP = 0.64\ cm^{-1}/kbar$.

Several lattice modes have been observed in the low-frequency ranges in the Raman spectra for 2-acetylpyrrole and they occur at 57, 64, 74, 98, 120, 125, 184 and 194 cm^{-1} respectively.

ACKNOWLEDGEMENTS

We would like to thank the FRD, CSIR (Pretoria) and the Council of the University of Pretoria for financial support.

REFERENCES

1. Jones R.A., Aust. J. Chem. 1963; 16 : 93
2. Khan M.K.A., Morgan K.J., J. Chem. Soc. 1964; 2597
3. Scott D.W., J. Mol. Spectroscopy 1971; 37 : 77

4. Cataliotti R., Gallina P., Paliani G., Spectroscopy Letters 1975; 8 : 799

5. Lord R.C., Miller F.A., J. Chem. Phys. 1942; 10 : 328

6. Emmert B., Brandl F., Chem. Ber. 1927; 60 : 2211

7. Emmert B., Diehl K., Gollwitzer F., Chem. Ber. 1929; 62 : 1733

8. Perry C.L., Weber J.H., J. Inorg. Nucl. Chem. 1971; 33 : 1031

9. Heyns A.M., Clark J.B., J. Raman Spectr. 1983; 14 : 342

10. English R.B., McGillivray G., Small E., Acta Cryst. 1980; B36 : 1141

11. Kaye P.T., Macrae R., Meakins G.D., Patterson C.H., J. Chem. Soc. Perkin Trans. II, 1980; 1631

Date Received: 07/09/87
Date Accepted: 08/11/87