Conformation of 4-Vinylpyridine in the Gas Phase. A Microwave Spectroscopic Investigation

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Abstract: The microwave spectrum of 4-vinylpyridine has been studied in the frequency region 18.0–26.5 GHz. The rotational transitions of the ground state and the first six torsionally excited states have been assigned. The ground state rotational constants have been determined to be A_0 = 5436.82 ± 0.11 MHz, B_0 = 1544.397 ± 0.002 MHz, and C_0 = 1204.700 ± 0.001 MHz. The molecule has been shown to be planar in the ground state. From intensity measurements, the frequency of the first torsional transition has been estimated to be 35 ± 15 cm^{-1}.

In the present paper the results of a study of the microwave spectrum of 4-vinylpyridine are reported. The investigation was undertaken in order to determine the conformation and torsional frequency of the 4-vinylpyridine molecule. This information is of particular value in view of the fact that no experimental structural determination or far-infrared investigation of 4-vinylpyridine has yet been reported. The present work also extends our previous microwave spectroscopic studies on vinyl derivatives of aromatic compounds.[1,2]

Experimental Section

The sample of 4-vinylpyridine was purchased from Riedel-de Haën and used without further purification. Microwave spectra were recorded using a Hewlett-Packard 8460A spectrometer equipped with a phase-stabilized source oscillator and with Stark modulation at 33.33 kHz. The measurements were performed in the frequency range 18.0–26.5 GHz (K band region) at room temperature and with sample pressures ranging from 10 to 60 mTorr.

Results and Discussion

Microwave Spectrum. In order to predict the microwave spectrum of 4-vinylpyridine an initial molecular structure was assumed. This structure was based on the substitution structure of pyridine[3] and on some calculated parameters for the vinyl group in styrene.[4,5] Using the rotational constants obtained in this way it was possible to make the assignment of the ground state lines within a few hours after the spectrum had been recorded. In Table I the measured frequencies as well as the transition frequencies of the ground state calculated from the final fit are listed. Some of the transitions with high K_{-1} values show detectable centrifugal distortion effects. These effects were, however, too small to permit accurate determination of the centrifugal distortion coefficients. Consequently, these lines were not included in the final fit of the rotational constants. On the high-frequency side of each ground state line a group of lines with regularly falling intensities was observed. These vibrational satellites were assigned to the torsional mode of vibration of the vinyl group. In Table II the measured rotational transition frequencies of six torsionally excited states are given. Only a-type R-branch transitions were identified in the spectrum. No splitting of the lines was observed, thus indicating a high barrier to internal rotation.

Molecular Constants. The rotational constants, calculated by a least-squares method, moments of inertia, and inertial defects for all vibrational species are given in Table III. The variation of the rotational constants with the torsional quantum number is illustrated in Figure 1. As can be expected from the results of previous investigations[1,2] a deviation from linear dependence is observed for the 4-vinylpyridine molecule. It should also be noted that the A constants of some torsional satellites, especially $v = 5$, are perturbed (cf. Figure 1a). It is possible that this perturbation may be due to Coriolis interaction. Figure 2 shows that the inertial defect is also nonlinear with the torsional quantum number.

Planarity of the Molecule. Had the potential function for the torsional vibration possessed a small maximum for the planar conformation, this would have resulted in the three rotational constants varying with the torsional quantum number in a zigzag pattern.[6] This type of behavior is not observed in the case of 4-vinylpyridine (cf. Figures 1b and 1c). Thus, this nonlinear dependence indicates an anharmonic torsional potential which has a minimum for the planar conformation. Moreover, extrapolation of the inertial defect to the hypothetically torsionless state $v = -\frac{1}{2}$ yields $\Delta_{-1/2} \approx 0.15$ amu Å^2. Such a small, positive value for the inertial defect is characteristic for planar molecules with small amplitude vibrations.[7] Therefore, it is concluded that the 4-vinylpyridine molecule is planar.

The large, negative inertial defect in the ground state ($\Delta_0 = -0.682$ amu Å^2) is interpreted as being caused by the low-lying torsional vibration of the vinyl group (cf. the section Torsional Vibration below). It should be mentioned that according to the usual theory of small amplitude vibrations[7,8] the inertial defect for a planar molecule is linearly dependent on the torsional quantum number. Deviations from linearity have, however, been reported for some planar benzene derivatives, e.g., benzoyl fluoride,[9] nitrobenzene,[10,11] *p*-fluorostyrene,[1] and *p*-chlorostyrene.[2] An exact reproduction of these deviations will, however, require further theoretical work.

Torsional Vibration. The frequency of the first torsional transition was obtained from approximate relative intensity measurements. The average intensity ratio of the first torsional satellite to the ground state was calculated from the intensities of ten selected line pairs. Then, using the Boltzmann distribution law, the corresponding energy difference was calculated to be 35 ± 15 cm^{-1}. This value can be compared with the value calculated from the change of the inertial defect with the vibrational quantum number. For a harmonic out-of-plane vibration, which possesses a much lower frequency than any in-plane vibration, the following formula has been derived:[11-13]

$$\nu_t = -\frac{h}{2\pi^2 c}\frac{1}{\Delta_1 - \Delta_0}$$

Inserting the values of the inertial defects of the ground (Δ_0) and first torsionally excited (Δ_1) states the corresponding torsional frequency becomes ν_t = 46 cm^{-1}. This value is in reasonable agreement with the value calculated from the intensity measurements. It should, however, be borne in mind that the torsional vibration of the vinyl group in 4-vinylpyridine is not harmonic as was demonstrated by the not-quite-linear dependence of the rotational constants on the torsional quantum number. A more detailed discussion of the torsional mode

Table I. Rotational Spectrum of 4-Vinylpyridine in the Ground State

Transition	Freq, MHz Obsd[a]	Freq, MHz Obsd − calcd	Transition	Freq, MHz Obsd[a]	Freq, MHz Obsd − calcd
$7_{0,7} \leftarrow 6_{0,6}$	18 254.83	0.05	$8_{2,6} \leftarrow 7_{2,5}$	23 073.17	−0.01
$7_{2,6} \leftarrow 6_{2,5}$	19 079.35	0.04	$9_{1,9} \leftarrow 8_{1,8}$	22 764.12	−0.01
$7_{2,5} \leftarrow 6_{2,4}$	20 065.02	0.04	$9_{0,9} \leftarrow 8_{0,8}$	23 023.56	−0.01
$8_{1,8} \leftarrow 7_{1,7}$	20 302.08	0.03	$9_{2,8} \leftarrow 8_{2,7}$	24 367.06	−0.03
$8_{0,8} \leftarrow 7_{0,7}$	20 646.82	−0.02	$9_{8,2} \leftarrow 8_{8,1}$ $9_{8,1} \leftarrow 8_{8,0}$	24 815.16[b]	0.21
$8_{2,7} \leftarrow 7_{2,6}$	21 736.07	0.02			
$8_{7,2} \leftarrow 7_{7,1}$ $8_{7,1} \leftarrow 7_{7,0}$	22 059.30[b]	0.21	$9_{7,3} \leftarrow 8_{7,2}$ $9_{7,2} \leftarrow 8_{7,1}$	24 827.93[b]	0.12
$8_{6,3} \leftarrow 7_{6,2}$ $8_{6,2} \leftarrow 7_{6,1}$	22 073.35[b]	0.17	$9_{6,4} \leftarrow 8_{6,3}$ $9_{6,3} \leftarrow 8_{6,2}$	24 847.89[b]	0.00
$8_{4,5} \leftarrow 7_{4,4}$	22 138.72[b]	0.07	$9_{3,6} \leftarrow 8_{3,5}$	25 279.83	−0.02
$8_{4,4} \leftarrow 7_{4,3}$	22 147.40[b]	−0.06	$9_{2,7} \leftarrow 8_{2,6}$	26 064.45	−0.02
$8_{3,6} \leftarrow 7_{3,5}$	22 154.24[b]	0.05	$10_{1,10} \leftarrow 9_{1,9}$	25 212.44	−0.03
$8_{3,5} \leftarrow 7_{3,4}$	22 352.11	0.01	$10_{0,10} \leftarrow 9_{0,9}$	25 398.57	−0.00
$8_{1,7} \leftarrow 7_{1,6}$	22 821.53	−0.01			

[a] ±0.05 MHz. [b] Not used in the final fit.

Table II. Rotational Transitions Frequencies (MHz) of 4-Vinylpyridine in the Torsionally Excited States

Transition	$v = 1$ Obsd[a]	$v = 1$ Obsd − calcd	$v = 2$ Obsd[a]	$v = 2$ Obsd − calcd	$v = 3$ Obsd[a]	$v = 3$ Obsd − calcd	$v = 4$ Obsd[a]	$v = 4$ Obsd − calcd	$v = 5$ Obsd[a]	$v = 5$ Obsd − calcd	$v = 6$ Obsd[a]	$v = 6$ Obsd − calcd
$7_{0,7} \leftarrow 6_{0,6}$	18 303.68	−0.03	18 336.38	0.01	18 366.16	0.03	18 392.96	0.13	18 416.80	0.07	18 439.09	0.04
$7_{2,6} \leftarrow 6_{2,5}$	19 121.89	0.02	19 149.39	0.01	19 173.91	−0.08	19 195.65	0.02	19 214.36	0.07	19 232.54	0.10
$7_{2,5} \leftarrow 6_{2,4}$			20 121.22	0.06	20 139.60	0.03	20 155.22	0.10				
$7_{1,6} \leftarrow 6_{1,5}$	20 135.68	0.08	20 157.71	0.01	20 176.98	0.03	20 193.26	0.09	20 207.22	0.07	20 220.46	0.01
$8_{1,8} \leftarrow 7_{1,7}$	20 361.34	0.01	20 401.19	0.02	20 437.67	0.02	20 470.77	0.04				
$8_{0,8} \leftarrow 7_{0,7}$	20 704.28	0.01	20 742.79	0.00	20 778.01	0.03	20 809.77	0.11	20 838.10	0.05	20 864.63	0.04
$8_{2,7} \leftarrow 7_{2,6}$	21 785.29	0.04	21 817.17	0.03	21 845.79	0.06	21 870.76	−0.14	21 892.61	−0.09	21 913.79	−0.01
$8_{3,5} \leftarrow 7_{3,4}$	22 396.18	−0.03	22 423.85	−0.05	22 448.27	−0.01			22 486.65	0.02	22 504.49	−0.07
$8_{1,7} \leftarrow 7_{1,6}$	22 863.50	−0.03	22 889.96	0.13	22 912.89	0.03	22 932.44	0.03	22 949.52	−0.00	22 965.50	0.00
$8_{2,6} \leftarrow 7_{2,5}$	23 112.18	0.02	23 135.79	−0.01	23 156.17	0.01	23 173.26	0.03			23 201.19	0.08
$9_{1,9} \leftarrow 8_{1,8}$	22 831.38	0.00	22 876.64	−0.01	22 918.15	0.01	22 955.78	−0.03	22 988.90	−0.00	23 020.90	0.09
$9_{0,9} \leftarrow 8_{0,8}$	23 089.55	0.01	23 133.92	−0.01	23 174.55	−0.01	23 211.33	0.06	23 244.07	−0.02	23 274.89	−0.03
$9_{2,8} \leftarrow 8_{2,7}$	24 423.13	−0.00	24 459.56	−0.02	24 492.29	−0.03			24 556.29	0.01	24 570.45	−0.01
$9_{3,6} \leftarrow 8_{3,5}$	25 328.32	−0.01	25 358.51	−0.05					25 426.28	0.00	25 445.65	−0.04
$9_{1,8} \leftarrow 8_{1,7}$	25 521.10	−0.04	25 552.00	−0.12	25 579.39	−0.03	25 602.61	−0.14	25 623.47	−0.05	25 642.50	−0.05
$9_{2,7} \leftarrow 8_{2,6}$	26 107.75	−0.02	26 133.98	0.01	26 156.46	−0.03	26 175.21	−0.06	26 190.27	−0.02		
$10_{1,10} \leftarrow 9_{1,9}$	25 287.76	−0.02	25 338.61	0.05			25 427.35	−0.11	25 464.69	0.00	25 500.47	−0.07
$10_{0,10} \leftarrow 9_{0,9}$			25 523.23	−0.04	25 569.27	−0.04	25 610.97	−0.04	25 648.14	−0.05	25 683.24	−0.04

[a] ±0.05 MHz.

Table III. Rotational Constants (MHz), Moments of Inertia (amu Å), and Inertial Defects for 4-Vinylpyridine in the Ground and Torsionally Excited States[b]

	$v = 0^a$	$v = 1$	$v = 2$	$v = 3$	$v = 4$	$v = 5$	$v = 6$
A	5436.82 ± 0.11	5415.71 ± 0.10	5399.67 ± 0.16	5383.71 ± 0.13	5366.72 ± 0.31	5356.08 ± 0.16	5339.09 ± 0.18
B	1544.3972 ± 0.0016	1546.1491 ± 0.0016	1547.0950 ± 0.0024	1547.8404 ± 0.0018	1548.3733 ± 0.0044	1548.7684 ± 0.0025	1549.1834 ± 0.0031
C	1204.6997 ± 0.0014	1208.8379 ± 0.0015	1211.6658 ± 0.0023	1214.2809 ± 0.0019	1216.6872 ± 0.0042	1218.7912 ± 0.0023	1220.8475 ± 0.0027
I_a	92.954	93.317	93.594	93.871	94.169	94.356	94.656
I_b	327.2319	326.8611	326.6613	326.5039	326.3916	326.3083	326.2209
I_c	419.5037	418.0676	417.0919	416.1937	415.3705	414.6535	413.9551
Δ	−0.682	−2.111	−3.163	−4.181	−5.190	−6.011	−6.922

[a] Asymmetry parameter $\kappa = -0.8395$. [b] The uncertainties represent one standard deviation. Conversion factor 505 376 MHz amu Å^2.

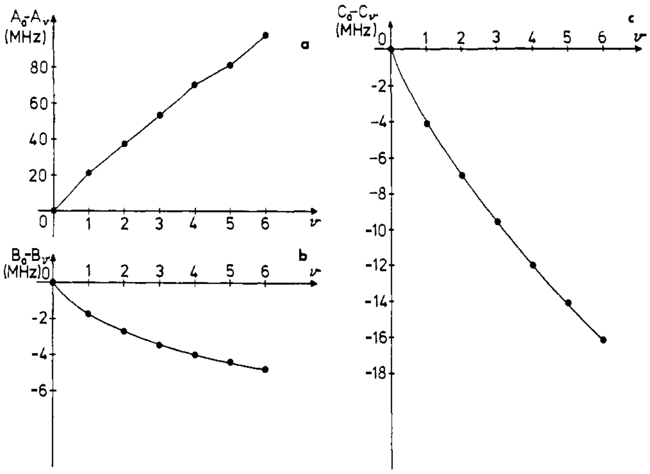

Figure 1. Variation of the rotational constants of 4-vinylpyridine with the torsional quantum number.

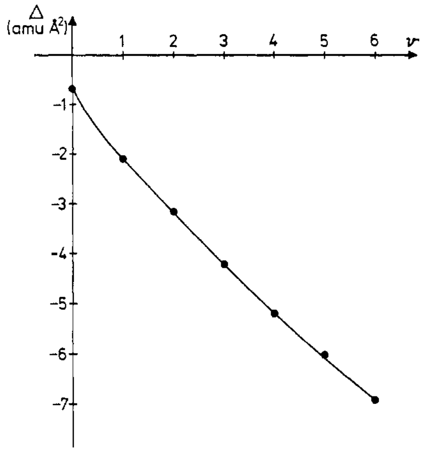

Figure 2. Variation of the inertial defect of 4-vinylpyridine with the torsional quantum number.

of vibration would require a careful far-infrared study, which is beyond the scope of the present paper.

It can be noticed that the torsional vibration of the vinyl group in 4-vinylpyridine as described in the present paper seems to be very similar to the corresponding vibrations in *p*-fluoro- and *p*-chlorostyrene.[1,2] This is not surprising since the relevant molecular fragments are nearly identical in these three molecules.

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References and Notes

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