The Microwave Spectrum of 2,6-Difluoropyridine

II. Dipole Moment, Quadrupole Coupling Constants and Vibrational Satellites

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Hyperfine splittings of rotational transitions of 2,6-difluoropyridine have been analysed to yield the ^{14}N quadrupole coupling constants. Their values are:

$$\chi_{aa} = 1.82 \pm 0.05 \text{ MHz}, \quad \chi_{bb} = -4.16 \pm 0.02 \text{ MHz}, \quad \chi_{cc} = 2.34 \pm 0.05 \text{ MHz}.$$

The electric dipole moment has been determined from Stark effects as $\mu = 3.82 \pm 0.06$ D, and satellites in the rotation spectrum have been correlated with the five lowest fundamental vibrations of this molecule.

The dipole moment, the quadrupole data and the structural differences between 2,6-difluoropyridine and pyridine itself can all be accounted for by the change in the electron distribution due to the fluorine substituents.

I. Introduction

In a previous paper [1], henceforth referred to as "part I", we have reported the complete structure of 2,6-difluoropyridine (2,6-DFP), as determined by double resonance modulation (DRM) microwave spectroscopy, and this work has yielded the first quantitative information about structural changes of the pyridine ring under substitution. An explanation of the observed contractions of ring bonds in terms of the electronic configuration within this molecule could not be given, however. To some extent, this unsatisfying situation can be remedied, since valuable information related to the electron distribution in molecules is derivable from electric dipole moments and from nuclear quadrupole coupling constants. We therefore completed the microwave study of 2,6-DFP with the determination of these two quantities. Their values, together with some data on low frequency vibrations, will be reported in the present paper, and the implications of the new data for the molecular structure will be discussed.

While the determination of the dipole moment and the quadrupole coupling constants were the chief aims of the present work, its sequence was dictated by the high probability of overlap between vibrational satellite transitions and the hyperfine multiplets of the ground state spectrum on the one hand, and by the experimental and computational complications which can arise in dipole determinations in the presence of quadrupole fine structure, on the other hand. Accordingly, the vibrational satellite spectra were completed first (Sect. III-A), as this allowed the selection of transitions that were not intermingled with satellites for the determination of the quadrupole coupling constants. Similarly, after the quadrupole analysis (Sect. III-B) had been completed, transitions with minimal hyperfine splittings could be selected for the determination of the electric dipole moment.

II. Experimental

Spectroscopic measurements on 2,6-DFP were made on a conventional Stark effect spectrometer [2] with a modulation frequency of 95 kHz. Stabilisation of the radiation sources and low-speed recording of the hyperfine multiplets was not considered necessary, and free-running, frequency-swept klystrons were used throughout. Absorptions were displayed on the oscilloscope. All measurements were conducted at room temperature and at gas pressures between 3 – 30 mTorr. Relative intensity measurements basically followed the method first described by Esbitt and Wilson [3].

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III. Results

A) Vibrational Satellite Spectra

According to investigations [4–6] by infrared and Raman spectroscopy, 2,6-DFP has five fundamental vibrations which, when excited to the first level, lead to easily observable satellites in the rotation spectrum with populations of ~10% or more of the ground state at $T \sim 300\,^\circ$K. The lowest vibrations are out-of-plane modes at 219 cm^{-1} = ν_{13} and at 247 cm^{-1} = ν_{18}, and these are followed by an in-plane vibration at 347 cm^{-1} = ν_{10}. For the next two modes at 460 cm^{-1} and 500 cm^{-1} differing interpretations have been proposed in the two i. r. studies [4, 5]; while the fundamental at 460 cm^{-1} was first interpreted [4] as in-plane mode, with the absorption at 500 cm^{-1} as out-of-plane vibration, a reversal of this assignment was later [5] suggested. Between 500 cm^{-1} and 700 cm^{-1} three more fundamental modes are expected, but only two of these have been identified in the i. r. studies.

Including the nine satellite spectra which had been identified as preparation for the structure determination (part I), a total of 22 satellites have been observed in the rotational spectrum. Twenty of these were fully assigned (Q- and R-branch) and 18 spectra could be fitted to the pseudorigid rotor Hamiltonian [9] used in part I. The latter group comprises seven fundamental vibrations, including the five lowest modes of vibration, and eleven satellite spectra arising from higher excited levels ($n > 1$) and combinations of the four lowest vibrations. Spectra associated with successive levels up to $n = 5$ of the lowest mode ($\nu_{13} = 219$ cm^{-1}) were identified in order to assess the detectability of rare isotopic forms (Part I, Sect. III-B-1). Transitions of the spectra corresponding to the levels $n = 3$ and $n = 4$ of this mode were found to deviate from the pseudorigid rotor pattern by up to ~5 MHz, but a detailed study of these effects was not undertaken.

Each satellite spectrum was assigned by DRM methods [7] through the identification of at least five Q-branch and between two and six R-branch transitions. From these data the complete spectra could be closely predicted and additional transitions were then measured by Stark spectroscopy. Final values of the rotational parameters were derived from all observed transitions [8] by least squares fits to the Hamiltonian [9] used previously. In these fits the distortion constants [9] τ_{aabb} and τ_{abab} were held fixed

Table 1a. Rotational parameters of satellite spectra due to fundamental vibrations of 2,6-difluoropyridine.

Satellite		Ground state [a]	$v_1 \equiv \nu_{13}$	$v_2 \equiv \nu_{18}$	$v_3 \equiv \nu_{10}$	$v_4 \equiv v_{17}$	$v_5 \equiv \nu_{27}$	$v_6 \equiv \nu_9$?	$v_7 \equiv \nu_{26}$?
Vibrational energy [b]		—	219 cm^{-1}	247 cm^{-1}	347 cm^{-1}	460 cm^{-1}	500 cm^{-1}	550 cm^{-1}?	~600 cm^{-1} [c]
Transitions fitted		23 R & 38 Q	8 R & 40 Q	11 R & 41 Q	8 R & 35 Q	6 R & 43 Q	5 R & 31 Q	8 R & 39 Q	3 R & 39 Q
A	in MHz	3747.701 (24) [d]	3745.70 (3)	3735.89 (2)	3757.18 (3)	3747.56 (3)	3748.21 (3)	3748.36 (3)	3741.52 (3)
B		1905.832 (12)	1905.09 (1)	1907.10 (1)	1906.79 (1)	1905.07 (1)	1906.71 (2)	1904.93 (2)	1905.42 (1)
C		1263.253 (11)	1264.20 (1)	1264.43 (1)	1262.56 (1)	1263.86 (1)	1261.95 (1)	1263.78 (2)	1263.39 (1)
τ_{aaaa} [e]	in kHz	−2.56 (30)	−2.73 (75)	−2.40 (63)	−2.60 (67)	−2.26 (63)	−3.01 (78)	−2.23 (90)	−2.22 (75)
τ_{bbbb}		−0.49 (6)	−0.48 (9)	−0.49 (6)	−0.48 (5)	−0.45 (5)	−0.55 (6)	−0.44 (8)	−0.44 (6)
I_a [f]	in μÅ^2	134.8496 (8)	134.292 (1)	135.276 (1)	134.509 (1)	134.855 (1)	134.831 (1)	134.826 (1)	135.072 (1)
I_b		265.1734 (18)	265.277 (2)	264.997	265.040 (1)	265.280 (2)	265.051 (2)	265.298 (3)	265.230 (2)
I_c		400.0593 (31)	399.759 (3)	399.687 (2)	400.278 (2)	399.866 (3)	400.473 (3)	399.893 (5)	400.017 (4)
I.D.		0.0363 (40)	−0.440 (4)	−0.586 (3)	0.728 (3)	−0.268 (4)	0.591 (4)	−0.231 (6)	−0.286 (5)

[a] From Ref. [1].

[b] From i.r. studies [4, 5] in conjunction with microwave intensity measurements.

[c] From microwave intensity measurements alone.

[d] Uncertainties (three times standard error) are given in units of the last digit quoted.

[e] $\tau_{aabb} = 0.35$ kHz and $\tau_{abab} = -0.47$ kHz for all satellite spectra (see text).

[f] Conversion factor: 5.05376×10^5 MHz μÅ^2.

to their respective values for the ground state spectrum, since they could not be determined with good accuracy from the transitions available. The rotational parameters of satellite spectra corresponding to fundamental vibrations are listed in Table 1 a, and those due to higher excited states and combination levels are collected in Table 1 b.

The correlation of individual satellites in the rotation spectrum with fundamental vibrations, as identified in the i.r. studies, was established through relative intensity measurements[3], and spectra due to higher excited states and combination levels were identified from the changes in the rotational constants with vibrational excitation. As the small population difference and the large frequency separations between corresponding rotational transitions of the two strongest satellites v_1 and v_2 rendered intensity comparisons between them often inconclusive, the correlation of v_1 and v_2 with i.r. frequencies was derived from intensity comparisons between the spectra $2\,v_1$ and $2\,v_2$ and between $3\,v_1$ and $3\,v_2$, for which the population differences are magnified by factors 2 and 3, respectively. Transitions from these four spectra and combinations between v_1 and v_2 were subsequently used to determine the relative populations and vibration frequencies corresponding to the spectra v_3 to v_7. These measurements resulted in a satisfactory correlation between the microwave and i.r. data for the five lowest fundamentals. The inertia defects[10] of the satellites v_4 and v_5, in particular, strongly support the interpretation[5] of $v_4 \equiv \nu_{17} = 460\ \mathrm{cm}^{-1}$ as out-of-plane vibration and $v_5 \equiv \nu_{27} = 500\ \mathrm{cm}^{-1}$ as in-plane mode. The satellites v_6 and v_7 correspond to fundamentals between $500\ \mathrm{cm}^{-1}$ and $700\ \mathrm{cm}^{-1}$, and the stronger spectrum v_6 is tentatively assigned to the in-plane mode $\nu_9 = 550\ \mathrm{cm}^{-1}$. The state v_7 lies $600 \pm 50\ \mathrm{cm}^{-1}$ above the ground state and it is not clear whether it should be interpreted as the in-plane mode $\nu_{26} = 567\ \mathrm{cm}^{-1}$ or as the out-of-plane vibration ν_{12} which has not been identified in the studies[4-6] by vibrational spectroscopy.

B) Quadrupole Coupling Constants

Approximate values of the coupling constants of 2,6-DFP were initially estimated by extrapolation of the constants of pyridine[11] and orthofluoropyridine[12]. The hyperfine patterns of transitions with $J < 10$ were then predicted[13], and the transitions with the largest splittings were selected for the determination of the coupling constants after their frequencies had been checked against the assigned satellite spectra in order to ensure that the hyperfine patterns were not falsified by overlap with satellite transitions. This procedure yielded about a dozen transitions with predicted splittings near 1 MHz for experimental examination. Naturally, special attention was focussed on the two $J = 1 \rightarrow 2$ transitions for which a total splitting of ~ 2 MHz could be expected. The results of the analysis, based on the usual first order treatment, are collected in Table 2a. They indicate:

$$\chi_{aa} = 1.82 \pm 0.05\ \mathrm{MHz}, \quad \chi_{bb} = -4.16 \pm 0.02\ \mathrm{MHz},$$
$$\chi_{cc} = 2.34 \pm 0.05\ \mathrm{MHz}.$$

As in pyridine, the C_{2v} symmetry of 2,6-DFP causes the orientation of the inertial axes (a, b, c) to coincide with the direction of the principal axes (x, y, z) of the electric field gradient tensor at the nitrogen atom. This allows a direct comparison of the coupling constants if, in accordance with the designation of axes in previous work[11, 12], one correlates the (a, b, c)- and (x, y, z)-systems of 2,6-DFP as $x \rightarrow c$, $y \rightarrow a$ and $z \rightarrow b$.

With the interpretation of coupling constants proposed by Townes and Dailey[14], and the specification of this theory for pyridine by Lucken[15], the differences in the electronic environment of the nitrogen atom in pyridine and 2,6-DFP can be assessed. In particular, the occupation number a of the atomic orbital p_x, which contributes to the π-bond system, and the occupation number b of the σ-bonds emerging from the sp^2-hybridised nitrogen atom are calculable from the expressions[15]:

$$-(1/2)\,a - (1/6)\,b = (\chi_{zz}/\chi_p) - (4/3) \qquad (1\,\mathrm{a})$$

and

$$(3\,\eta - 9)\,a + (\eta + 9)\,b = 8\,\eta \qquad (1\,\mathrm{b})$$

where

$$\eta = (\chi_{yy} - \chi_{xx})/\chi_{zz} \qquad (1\,\mathrm{c})$$

and χ_{p} is the field gradient due to a single unbalanced $2\mathrm{p}_z$ electron, which for nitrogen is commonly assumed as -10 MHz. Finally, as the quantities $a - 1 = i_\pi$ and $b - 1 = i_\sigma$ represent the ionicity of the nitrogen π- and σ-bonds, respectively, the excess charge at the nitrogen atom can be obtained as

$$c = i_\pi + i_\sigma = a + 2\,b - 3\,. \qquad (2)$$

Clearly, as long as one is interested primarily in a comparison, – rather than in the absolute values –,

Table 1 b. Rotational parameters of satellites arising from higher

Satellite Vibrational energy [c] Transitions fitted		$2\,v_1$ $\sim$440 cm^{-1} 8 R & 37 Q	v_1+v_2 $\sim$465 cm^{-1} 9 R & 39 Q	$2\,v_2$ $\sim$495 cm^{-1} 9 R & 29 Q	v_1+v_3 $\sim$565 cm^{-1} 6 R & 27 Q	v_2+v_3 $\sim$595 cm^{-1} 2 R & 18 Q	$3\,v_1$ [a] $\sim$660 cm^{-1} 7 R & 19 Q
A	in MHz	3743.69 (4) [d]	3734.16 (2)	3724.87 (4)	3754.71 (3)	3745.31 (4)	3741.8 (6)
B		1904.35 (2)	1906.36 (2)	1908.32 (1)	1906.03 (1)	1908.10 (2)	1903.8 (4)
C		1265.14 (1)	1265.37 (2)	1265.54 (1)	1263.53 (1)	1263.81 (1)	1266.1 (3)
τ_{aaaa} [e]	in kHz	−3.09 (99)	2.3 (13)	−2.3 (11)	−2.62 (90)	−4.3 (62)	−2.56 (a)
τ_{bbbb}		−0.49 (9)	−0.48 (12)	−0.48 (9)	−0.45 (7)	−0.6 (7)	−0.49 (a)
I_a [f]	in μÅ^2	134.994 (1)	135.338 (2)	135.676 (1)	134.598 (1)	134.936 (1)	135.06 (2)
I_b		265.379 (2)	265.099 (3)	264.827 (2)	265.145 (2)	264.858 (2)	265.46 (6)
I_c		399.461 (4)	399.389 (5)	399.337 (3)	399.971 (3)	399.883 (3)	399.16 (7)
I.D.		−0.912 (5)	−1.049 (6)	−1.166 (4)	0.227 (4)	0.089 (4)	−1.36 (9)

[a] High-J Q-branch transitions of this spectrum deviate from the pseudo-rigid rotor pattern by up to 5 MHz. The distortion

[b] Spectrum shows similar features as $3\,v_1$, but of smaller magnitude.

[c] Estimated from i.r. values for fundamentals.

[d-f] as in Table 1 a.

of the electron distribution parameters a, b and c, the reservations[16] arising from approximations in the Townes-Dailey theory and those connected with the assumed population number 2 of the lone pair orbital $\Psi_{\sigma z}$ (i.e. the uncertainty in the assumed value of χ_{p}) are of little concern. However, the derivation of Eq. (1) also implies a value of 120° for the angle between the three σ-bonds in the plane of the ring, while the bond angle CNC is known to be 117° in pyridine and 115° in 2,6-DFP (which suggests an angle of CNC = 116° for orthofluoropyridine). Hence, in order to ensure first that the trends in the electron distribution parameters along the series: pyridine, orthofluoropyridine, 2,6-DFP are not wholly due to the neglect of the increasing deviation of the CNC bond angle from 120°, we have repeated the calculation of a, b and c [using Eq. (4) with $\varepsilon = 0$] taking into account the observed bond angles and the decreasing s-character in the σ-bonds. This latter quantity was calculated from the relation[17a]

$$s = \cos \text{CNC}/(\cos \text{CNC} - 1)\ . \tag{3}$$

As both these calculations lead to unreasonably large charges at the nitrogen atom, a third calculation was carried out in which the shielding[17b] of the quadrupolar nucleus by the excess charge was taken into consideration. In this case, Eq. (1) takes the form

$$[2\,s - (1/2)]\,b + (1/2)\,a = 4\,s - (\chi_{zz}/\chi_{\text{p}})\,(1 + \varepsilon\,c) \tag{4 a}$$

and

$$b - a = (2/3)\,\eta\,(\chi_{zz}/\chi_{\text{p}})\,(1 + \varepsilon\,c) \tag{4 b}$$

with η, c and s defined in Eq. (1 c), (2) and (3), and $\varepsilon = 0.3$[17b].

The results of these calculations are collected in Table 2 b and may be summarised as follows:

1) All three methods of calculation indicate a marked increase of the occupation number a of the π-orbital.
2) While a small increase of the population b of the σ-bonds is obtained in the crudest approach (CNC = 120°, $\varepsilon = 0$), a small decrease of b is calculated when the changing s-character and CNC angles are taken into consideration.
3) All three electron distribution parameters are significantly reduced if the shielding of the nitrogen nucleus by the excess charge is taken into account.
4) As a result of the increase of the population of the π-orbital (0.102 e) in combination with the only small decrease of the population of the σ-orbital (− 0.015 e), an increase of the excess charge at the nitrogen atom (0.071 e) from 0.520 e in pyridine to 0.591 e in 2,6-DFP is obtained.

This final result is an agreement with the concept that the fluorine atom acts as an electron donor to the π-bonds while withdrawing electrons from the σ-bonds. In the present case however, the latter effect appears to be an order of magnitude smaller than the former, so that a net increase of the electron density at the nitrogen atom is produced when the ortho hydrogens are replaced by fluorine.

excited states and combinations of the four lowest modes.

v_1+v_4 ~680 cm^{-1} 3 R & 14 Q	$2\,v_1+v_2$ 685 cm^{-1} 3 R & 24 Q	$2\,v_3$ 690 cm^{-1} 2 R & 12 Q	$v_1+2\,v_2$ 710 cm^{-1} 2 R & 17 Q	$3\,v_2$ 740 cm^{-1} 3 R & 12 Q	$4\,v_1$ [b] 880 cm^{-1} 4 R & 15 Q	$5\,v_1$ 1100 cm^{-1} 2 R & 17 Q
3745.62 (9)	3732.41 (4)	3765.6 (2)	3723.33 (3)	3714.49 (7)	3739.54 (9)	3737.6 (2)
1904.35 (7)	1905.64 (2)	1907.73 (9)	1907.58 (1)	1909.51 (3)	1902.90 (2)	1902.30 (6)
1264.76 (5)	1266.30 (2)	1261.99 (6)	1266.47 (1)	1266.60 (2)	1266.99 (1)	1267.94 (5)
−3.3 (37)	−2.3 (11)	−4.5 (55)	−1.78 (84)	−1.1 (17)	−0.6 (23)	−2.9 (42)
−0.8 (4)	−0.4 (1)	−0.61 (48)	−0.41 (8)	−0.43 (14)	−0.33 (15)	−0.73 (30)
134.924 (4)	135.402 (2)	134.208 (8)	135.732 (1)	136.055 (3)	135.144 (4)	135.213 (7)
265.380 (9)	265.200 (3)	264.909 (13)	264.931 (2)	264.663 (4)	265.581 (3)	265.666 (9)
399.580 (17)	399.096 (5)	400.459 (22)	399.044 (4)	399.003 (6)	398.878 (4)	398.581 (16)
−0.721 (21)	−1.506 (6)	1.342 (26)	−1.619 (5)	−1.715 (8)	−1.484 (6)	−2.298 (20)

constants were assigned ground state values for the least squares fit.

Table 2 a. Calculated and observed splittings between nuclear hyperfine components in 2,6-difluoropyridine.

Transition	Hyperfine components		Splittings (in MHz)	
	$F \rightarrow F+1$	$F' \rightarrow F'+1$	$\lvert\Delta\nu\rvert_{\text{calc}}$	$\lvert\Delta\nu\rvert_{\text{obs}}$
$2_{11} \rightarrow 3_{22}$	$2 \rightarrow 3$	$3 \rightarrow 4$	1.337	1.334
	$3 \rightarrow 4$	$1 \rightarrow 2$	0.742	0.739
	$2 \rightarrow 3$	$1 \rightarrow 2$	2.080	2.073
$2_{12} \rightarrow 3_{21}$	$1 \rightarrow 2$	$3 \rightarrow 4$	0.676	0.662
	$3 \rightarrow 4$	$2 \rightarrow 3$	1.490	1.480
	$1 \rightarrow 2$	$2 \rightarrow 3$	2.166	2.142
$4_{22} \rightarrow 5_{33}$	$4 \rightarrow 5$	$5 \rightarrow 6$	0.960	0.958
	$5 \rightarrow 6$	$3 \rightarrow 4$	0.264	0.228
	$4 \rightarrow 5$	$3 \rightarrow 4$	1.224	1.196
$4_{13} \rightarrow 5_{24}$	$4 \rightarrow 5$	$5 \rightarrow 6$	1.109	1.101
$6_{24} \rightarrow 7_{35}$	$6 \rightarrow 7$	$7 \rightarrow 8$	1.056	1.058
$6_{33} \rightarrow 7_{44}$	$6 \rightarrow 7$	$7 \rightarrow 8$	0.667	0.699
	$7 \rightarrow 8$	$5 \rightarrow 6$	0.124	
$8_{26} \rightarrow 9_{37}$	$8 \rightarrow 9$	$9 \rightarrow 10$	0.819	0.873
	$9 \rightarrow 10$	$7 \rightarrow 8$	0.109	
$10_{8.2} \rightarrow 10_{9.1}$	$10 \rightarrow 10$	$11 \rightarrow 11$	0.381	0.354
$10_{2.8} \rightarrow 11_{3.9}$	$10 \rightarrow 11$	$11 \rightarrow 12$	0.429	0.434

$\chi_{aa} = 1.82 \pm 0.05$ MHz; $\chi_{bb} = -4.16 \pm 0.02$ MHz; $\chi_{cc} = 2.34 \pm 0.05$ MHz

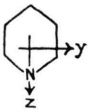
C) Dipole Moment

The comparatively large weight, the asymmetry and the vibrational satellites of 2,6-DFP naturally lead to a relatively dense microwave spectrum. Since, in addition, the quadrupole fine structure and the small intensity of low-J lines further reduced the number of transitions that could be hoped to be usable for the dipole determination, it was necessary to examine many transitions for resolved Stark components. Unfortunately, while the Stark lobes of transitions with medium J-values ($5 < J < 10$) were not sufficiently well resolved, those of the low-J transitions without hfs were mostly weak and too 'fast' for comparison with OCS. Thus, despite considerable effort, only one transition ($3_{22} \rightarrow 4_{31}$) was found which showed all the characteristics desirable for a dipole determination (three resolved lobes, Stark coefficients comparable with OCS, no hfs, no interference from neighbouring transitions or their Stark effects). Fortunately, the transition $15_{5,11} \rightarrow 15_{6,10}$ had been noted earlier to exhibit a single Stark lobe of the same intensity as the zero-field absorption, which indicated that the coefficient B in the expression $\Delta\nu/E^2 = A + B\,M^2$ [giving the displacement $\Delta\nu$ of an individual M-component as function of the electric field E [18]] was so small as to make all 15 M-components coalesce up to fields of ~1000 V/cm. A similar situation was eventually discovered for the transition $4_{40} \rightarrow 5_{51}$, bringing the number of readily analysable Stark lobes to five.

The Stark coefficients ($\Delta\nu/E^2$) of the five lobes were measured in the usual manner, with the square-wave generator calibrated against the two lobes of the $J = 1 \rightarrow 2$ transition of OCS ($\mu_{\text{OCS}} = 0.71521$ D [19]). The second order Stark effect was calculated by the method of Golden and Wilson [18], and the dipole moment was then derived from each of the five lobes. This resulted in an average value of $\mu = \mu_b = 3.82 \pm 0.06$ D. A comparison between the observed Stark coefficients and those calculated with this average value is given in Table 3.

A definite correlation of the observed dipole moment of 2,6-DFP with the moment, and hence the electron distribution, of the unsubstituted portion of the ring alone is not possible, since the total dipole moment contains a contribution due to the replacement of two C – H moments by C – F bond moments,

Table 2b. Comparison between quadrupole coupling constants and deduced electron distributions at the nitrogen atom in pyridine, orthofluoropyridine and 2,6-difluoropyridine.

	Pyridine[11]	Orthofluoro-pyridine[12, 27]	2,6-difluoro-pyridine
Coupling constants (in MHz)			
 χ_{xx}	3.47	2.82	2.34
χ_{yy}	1.40	1.68	1.82
χ_{zz}	−4.87	−4.50	−4.16
η	0.425	0.253	0.125
Electron distributions			
I. CNC-angle = 120°, shielding neglected [Eq. (1)]			
a	1.235	1.306	1.367
b	1.373	1.382	1.402
c	0.981	1.070	1.171
II. Observed CNC-angles included, shielding neglected [Eq. (4) with $\varepsilon=0$]			
∢ CNC	117°	116°	115°
s	0.3112	0.3048	0.2971
a	1.193	1.248	1.294
b	1.331	1.324	1.329
c	0.854	0.896	0.952
III. Observed CNC-angles and shielding included [Eq. (4) with $\varepsilon=0.3$] (CNC-angles and s as in II.)			
a	1.067	1.124	1.169
b	1.226	1.213	1.211
c	0.520	0.549	0.591

and this contribution can not be fixed accurately. Nevertheless, some qualitative conclusions concerning the change of the dipole moment of the ring itself can still be drawn. Thus, if the polarity of the unsubstituted part of 2,6-DFP were the same as in pyridine, a moment of 1.52 D along the C – F bonds would have to be inferred. This follows from the moment of pyridine (2.22 D) in combination with the known angle between the C – F bonds and the C_2 symmetry axis (58.2°, Part I, Figure 3). As this moment would be 0.1 – 0.2 D larger than the corresponding moments in vinyl fluoride[20], *cis*-difluoroethylene[21] and trifluoroethylene[22] (1.42 D, 1.43 D and 1.32 D, respectively) it appears very probable that the unsubstituted portion of 2,6-DFP is more polar than the corresponding portion of the pyridine molecule. This conclusion agrees with the interpretation of the quadrupole data.

For a crude estimate of the polarity of the ring two approaches are open: If, in view of the dipole moments in fluoroethylenes, one assumes that the replacement of one C – H by a C – F bond produces a moment of 1.37 ± 0.05 D in the direction of the C – F bond, the contribution from two such moments to the total moment of 2,6-DFP is calculated as $2(1.37 \pm 0.05) \cos 58.2 = 1.44 \pm 0.06$ D, and the moment of the unsubstituted portion alone is then 3.82 D – 1.44 D = 2.38 D. Alternatively, one may start out from the crude assumption that the ring moment should be proportional to the excess charge c at the nitrogen atom, as determined from the quadrupole data. In this case, as the increase of c in 2,6-DFP stems largely from the increased π-bond occupation, the π-moment of 2,6-DFP would be estimated from that of pyridine ($\mu_\sigma = 0.86$ D, $\mu_\pi = 1.36$ D[23]) as

$$\mu_{\pi,\,2,6\text{-DFP}} = \mu_{\pi,\,\text{Pyr.}} \times (c_{2,6\text{-DFP}}/c_{\text{Pyr.}}) = 1.36 \times (0.59/0.52) = 1.54\ \text{D}\,.$$

By addition of the assumedly unchanged σ-moment of pyridine to this value, the ring moment of 2,6-DFP would then be obtained as 2.40 D, in good agreement with the value derived above from a different assumption. In combination with the observed moment of 2,6-DFP, this value for the ring moment would require a component of 1.35 D along the direction of each C – F bond.

From these considerations it is seen that the assumption of a slightly smaller value than in vinyl fluoride and *cis*-difluoroethylene for the moment along the C – F bonds in 2,6-DFP leads to a moment for the unsubstituted portion of the ring which is in good agreement with the quadrupole data. The suggested division of this moment (2.40 D) into π- and σ-components (1.54 D and 0.86 D) has to remain open to revision, since it is based on the electron distribution at the nitrogen atom alone without changes at the C(2/6) and C(3/5) atoms being taken into account.

IV. Discussion

As stated in Part I and Sect. I above, our prime motive for the study of vibrational satellite spectra of 2,6-DFP (Sect. III-A) was to facilitate the identification of isotopic species spectra and the quadrupole analysis by eliminating satellite transitions as a possible source of confusion or misinterpretation. While this part of the work could hardly be considered a preparatory measure if attempted by Stark spectroscopy, the efficiency of DRM methods for the identification of satellite spectra made this approach well worth the little effort it required. As we had no difficulty in detecting the ^{15}N spectra in their natural abundance (see Part I, Fig. 2 b), there can be no doubt that the associated rotation spectra of more than half of the 27 fundamental vibrations of 2,6-DFP could be observed by DRM spectroscopy if the resulting data were of specific importance. As there is nearly complete consistency between the two i.r. studies on this molecule, we saw no reason to continue the investigation to beyond the limits set by our original concern, and we therefore terminated the study of excited vibration states after the identification of the fundamentals up to 500 cm^{-1}.

The chief results of the present investigation are the dipole and the quadrupole data (Sect. III, B and C). These provide a good deal of information on the electron distribution which, in turn, can be used to explain the structural differences between pyridine and 2,6-DFP, as determined in Part I of this study. Thus, on the basis of the quadrupole data the shortening of the N – C bonds in 2,6-DFP must be ascribed to an influx of electrons into the π-sections of these bonds and the additional charge at the nitrogen atom must originate from the fluorine atoms. The very probable reduction of the C – F bond moment in comparison to fluoroethylenes would seem to support this view.

While the quadrupolar nitrogen nucleus provides a convenient probe for exploring the electron distribution in the N(1) – C(2/6) bonds (see Fig. 3 of Part I for numbering of atoms), no comparable information about the electron distribution at the C(3/5) atoms can be extracted from the present data. One is therefore limited to indirect evidence in assessing the electronic environment of these atoms: Either, it may be assumed that the charge released by the fluorine atoms is distributed between the nitrogen and C(3/5) carbon atoms in the ratio of their electronegativities (3.0 and 2.6, respectively), or one may postulate proportionality between the contraction of the bonds and the increase in electron density with respect to pyridine. In 2,6-DFP both these approaches lead to the same result. With a charge increase at the nitrogen atom of $\delta c = (0.59 - 0.52)/2 = 0.035$ e, as determined from the quadrupole data (Table 2 b), the charge increase at the C(3/5) atoms is calculated from the electronegativities of C and N as

$$\delta c(3/5) = 0.035 \times (2.6/3.0) = 0.030\,\text{e}\,,$$

while the bond contractions of 0.021 Å and 0.017 Å for the N(1) – C(2/6) and C(2/6) – C(3/5) bonds, respectively, suggest

$$\delta c(3/5) = 0.035 \times (0.017/0.021) = 0.028\,\text{e}\,.$$

Table 3. Stark effects in 2,6-difluoropyridine.

Transition	$\Delta\nu/E^2$ in (MHz×10^6)/(V/cm)^2	
	Calc.	Obs.
$3_{22}-4_{31}$		
$M = 0$	−3.279	−3.21
$M = 1$	−1.712	−1.67
$M = 2$	2.986	3.01
$4_{40}-5_{51}$		
$M = 0$	−22.90	−23.3
$M = 4$	−23.00	
$15_{5,11}-15_{6,10}$		
$M = 15$	10.96	11.04
$\mu = \mu_b = 3.82 \pm 0.06$ D		

From these considerations it would appear that each fluorine atom injects ~0.06 e into the π-bond system of the ring, but it must also be remembered that, while acting as a π-donor, fluorine is a σ-acceptor. As the quadrupole data indicate no appreciable withdrawal of σ-electrons from the nitrogen atom, a similar situation has probably to be inferred for the C(3/5) atoms, and this leaves only the C(2/6) atoms as the source from which the adjacent fluorine atom could withdraw σ-electrons. Also, if the double bond character in the C(2/6)-F bonds in 2,6-DFP were to be in line with that suggested for orthobromo- and orthochloropyridine[24, 25] (4.8% and 4.0%, respectively), the withdrawal of σ-electrons from each C(2/6) atom would have to be ~0.055 e if the π-density at these atoms had increased by an amount comparable to that at the nitrogen atom (or by ~0.025 e if the π-density at C(2/6) had remained the same as in pyridine). In contrast to the explanation proposed for the shortening of ring bonds observed for the pair: benzene/fluorobenzene[26], we thus arrive at the conclusion that the corresponding contraction of bonds in the pair: pyridine/2,6-DFP results most probably from an increase in the electron density in the π-sections of the C – N and C – C bonds, and that this increase outweighs by a factor of ~2 the withdrawal of σ-electrons from the carbon atoms which carry the substituent.

Since the microwave data do not allow further checks of this hypothesis, we have compared the ^{13}C n.m.r. spectra of pyridine and 2,6-DFP. These reveal indeed an up-field shift of the signals due to the C(3/5) atoms (+17.7 ppm) and a down-field displacement for the C(2/6) carbon atoms (–12.2

ppm) in 2,6-DFP. Although a quantitative interpretation of these shifts in terms of the electronic environments of the two carbon atoms falls clearly outside the scope of the present study, these data appear to provide qualitative support for the explanation proposed above for the structural differences between pyridine and 2,6-DFP.

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[1] O. L. Stiefvater, Z. Naturforsch. **30 a**, 1765 [1975], Part 1.

[2] R. H. Hughes and E. B. Wilson, Jr., Phys. Rev. **71**, 562 [1947].

[3] A. S. Esbitt and E. B. Wilson, Jr., Rev. Sci. Instrum. **34**, 901 [1963].

[4] R. T. Bailey and T. Steele, Spectrochim. Acta **23 A**, 2997 [1967].

[5] J. H. S. Green, D. J. Harrison, and M. R. Kipps, Spectrochim. Acta **29 A**, 1177 [1973].

[6] S. Lui and J. A. Ladd (to be published).

[7] O. L. Stiefvater, DRM, Part III (unpublished).

[8] Listings of the observed transitions may be obtained from the authors.

[9] P. Nösberger, A. Bauder, and Hs. H. Günthard, Chem. Physics **1**, 426 [1973].

[10] D. R. Herschbach and V. W. Laurie, J. Chem. Phys. **40**, 3142 [1964].

[11] G. O. Sørensen, L. Mahler, and N. Rastrup-Andersen, J. Mol. Structure **20**, 119 [1974].

[12] S. D. Sharma, S. Doraiswamy, H. Legell, H. Mäder, and D. Sutter, Z. Naturforsch. **26 a**, 1342 [1971].

[13] Computer programme ASQU by A. Bauder (E.T.H. Zürich).

[14] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 [1949].

[15] E. A. Lucken, Trans. Faraday Soc. **57**, 729 [1961].

[16] E. Schempp and P. J. Bray, J. Chem. Phys. **49**, 3450 [1968].

[17] a) C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill Book Co., New York 1955, p. 243; b) ibidem, p. 238, 239.

[18] S. Golden and E. B. Wilson, Jr., J. Chem. Phys. **16**, 699 [1948].

[19] J. S. Muenter, J. Chem. Phys. **48**, 4544 [1968].

[20] D. R. Lide, Jr., and D. Christensen, Spectrochim. Acta **17**, 665 [1961].

[21] V. W. Laurie and D. T. Pence, J. Chem. Phys. **38**, 2693 [1963].

[22] O. L. Stiefvater, Ph.D., Thesis, Birmingham 1965.

[23] L. E. Orgel, T. L. Cottrell, W. Dick, and L. E. Sutton, Trans. Faraday Soc. **47**, 113 [1951].

[24] W. Caminati and P. Forti, Chem. Phys. Letters **15**, 343 [1972].

[25] F. Scappini and A. Guarnieri, Z. Naturforsch. **27 a**, 1011 [1972].

[26] L. Nygaard, I. Bojesen, T. Pedersen, and J. Rastrup-Andersen, J. Mol. Structure **2**, 209 [1968].

[27] The constants χ_{yy} and χ_{zz} of Ref. [12] are obtained from assumptions which we consider unjustified. Since the microwave- and NQR-values (Ref. [16]) for χ_{zz} differ by 0.30 MHz in pyridine, we prefer for orthofluoropyridine $\chi_{zz}(\text{gas}) = \chi_{zz}(\text{NQR}) - 0.30\ \text{MHz} = -4.50\ \text{MHz}$.